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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

3595. **Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1959, **35**, 605–607.—Automatic methods for the determination of C and H in organic compounds are reviewed. Electrical relay control systems, and the use of a high-frequency induction heater instead of an electric furnace, are discussed. (18 references.) S.C.I. Abstr.

3596. **Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 35–37.—Mercurimetric methods for the determination of chloride are specially discussed, the disadvantages of argentimetric methods being briefly summarised. Diphenylcarbazone as indicator gives a deep violet complex with Hg^{2+}, but the pH of the reaction is important; the use of bromophenol blue as a screen is recommended so that the test solution can be adjusted to the correct pH before commencing titration. Carbazide derivatives are also discussed. (24 references.) S.C.I. Abstr.

3597. **Development of metallurgical spectroscopy.** E. H. S. van Someren. *J. Iron St. Inst.*, 1960, **194** (1), 51–53.—A review. J. W. O. Pyemont

3598. **Some theoretical considerations in analytical chemistry. II. Discriminants in ion combination reaction calculations.** E. Bishop (Washington Singer Lab., Univ., Exeter, England). *Anal. Chim. Acta*, 1959, **21** (6), 493–502 (in English).—The use of discriminants is proposed to place on a simple quant. basis the selection of the appropriate equation for an analytical calculation for which alternative equations of different degrees of exactitude present themselves. Sufficient examples of discriminants are given to permit the direct treatment of the commoner calculations in titrimetric analysis, and to afford a pattern for their derivation whenever a choice of alternative equations is offered.

III. Importance of the ionisation of the weak acid or base in buffer media calculations. E. Bishop. *Ibid.*, 1960, **22** (1), 16–22.—The equation $[H^+] = K_a \times [acid]/[salt]$ assumes that the ionisation of the acid is negligible, and significant errors can arise from the use of this simplified expression. Errors result similarly from the correspondingly simplified equation for basic buffer soln. Graphical data are presented to demonstrate the magnitude of these errors. R. E. E.
H. N. S.

3599. **A least-squares method for multi-component analyses.** R. P. Bauman (Polytech. Inst. of Brooklyn, N.Y., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (6), 156–157.—A mathematical treatment of the results is shown to cut down the number of extinction measurements required in an analysis. A worked example is shown for the analysis of a mixture of ethylbenzene and *p*-xylene by extinction measurements at three frequencies only. P. T. Beale

3600. **Simplified equations for fitting least-square lines to data.** J. Deutschberger and A. Kirshbaum (Food Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (12), 752–754.—A simple general method for calculating the best dose-response line in microbiological assays is given, with the assay of novobiocin as an example.
W. H. C. Shaw

3601. **Synthetic and analytical studies on colour reagents. VIII. o-Halogeno-o′-hydroxyazo compounds.** Tadashi Iwachido, Haruo Miyata and Kyoji Toei (Chem. Dept., Fac. of Sci., Okayama Univ. Tsushima, Okayama). *Bull. Chem. Soc. Japan*, 1960, **33** (1), 95–98.—*o*-Halogeno-*o*′-hydroxyazo compounds are prepared and their identification limits for Ca, Mg and Th are determined. The absorption spectra of *o*-halogenophenylazochromotropic acids and their Mg complexes are given, and the relationship between the absorption spectra and their structures is discussed. I. Jones

3602. **Studies in qualitative inorganic analysis. XIV. Separation of the zinc-group sulphides.** D. Bailey and W. M. Dowson (Dudley Tech. Coll., Staffs., England). *Mikrochim. Acta*, 1960, (1), 12–16 (in English).—An improved separation of Zn, Mn, Ni and Co can be achieved by a selective pptn. of the Zn as sulphide from *N* acetic acid soln. The mixed sulphides are dissolved in aqua regia and the soln. is evaporated to dryness. The residue is dissolved in *N* acetic acid and Zn is pptd. with H_2S; Mn is pptd. from the filtrate as MnO_2 with aq. NH_3 and aq. Br soln., and Ni and Co are detected in two separate portions of the filtrate from the Mn pptn. by colour reactions.
W. T. Carter

3603. **Use of brucine as a redox indicator in dichromate titrations.** G. Gopala Rao and T. P. Sastri (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1960, **172** (1), 28–32 (in English).—Bivalent iron is titrated to a pink end-point with 0·5 *N* to 0·1 *N* $K_2Cr_2O_7$ in 3 to 4 *N* H_2SO_4, with 1 ml of 0·1% brucine soln. in 3 *N* H_2SO_4 or acetic acid as indicator. Quinol can be titrated in 5 *N* H_2SO_4 at room temp. A correction of 0·02 ml has to be made in titrations with 0·01 *N* $K_2Cr_2O_7$. The titration of U^{IV} is carried out in the cold in 4 *N* H_2SO_4. Typical results for Fe^{II}, quinol and U^{IV} are given. B. B. Bauminger

3604. **Variamine blue sulphate as redox indicator.** L. Erdey, E. B.-Gere and É. Bányai (Inst. for General Chem., Tech. Univ., Budapest). *Talanta*, 1959, **3** (2), 209–210 (in English).—The preparation of Variamine blue sulphate is described. It is more easily prepared than the free base, more stable than either the base or the hydrochloride, and can be used as a solid indicator (in a 1:400 mixture with

anhyd. Na_2SO_4) or as a 1% aq. soln. for those determinations in which the presence of Cl^- in the indicator has to be avoided, *e.g.*, the argentimetric determination of Cl^-. G. BURGER

3605. **Non-logarithmic linear titration curves.** B. H. J. Hofstee (Res. Foundation, Palo Alto, Calif.). *Science*, 1960, **131**, 39.—Titration curves can be based on linear non-logarithmic forms of the equilibrium equation of a dissociation reaction. From such curves, in contrast to those based on logarithmic transformations, both the end-point of the titration and the dissociation constant can be deduced. N. E.

3606. **Fundamentals of the use of non-aqueous solvents in acid-base titration.** N. A. Izmailov. *Zavod. Lab.*, 1960, **26** (1), 29–41.—A theoretical study and a review with 81 references is presented. G. S. SMITH

3607. **Quantitative oxidations by potassium ferricyanide.** Bharat R. Sant and Suseela B. Sant (Univ., Toronto, Canada). *Talanta*, 1960, **3** (3), 261–271 (in English).—A critical review is made of the many titrimetric procedures with potassium ferricyanide (**I**) as oxidant for the determination of, *e.g.*, VO^{2+}, Tl^+, Hg^+, Ce^{3+}, Co^{2+}, As^{3+}, sulphur compounds, ascorbic acid, reducing sugars, hydrazine, hydroxylamine and cysteine. The methods comprise (*i*) oxidation by excess of **I**, the excess being determined iodimetrically or the ferrocyanide formed being titrated with $Ce(SO_4)_2$, (*ii*) direct titration of **I** with the reducing agent, a potentiometric end-point being nearly always possible; no indicator is required if the titration can be made in the presence of $ZnSO_4$. (86 references.) W. J. BAKER

3608. **Complexones. XXXI. [N-(2-Hydroxycyclohexyl)ethylenediamine-NN'N'-triacetic acid.** J. Schubert, G. Anderegg and G. Schwarzenbach (Eidg. Tech. Hochschule, Zürich). *Helv. Chim. Acta*, 1960, **43** (1), 410–413 (in German).—The stability constants have been determined for the complexes of seven metals with this compound and compared with those for the ethylenediamine- and hydroxyethylenediamine-tetra-acetic acid complexes. The introduction of the *cyclo*hexyl group increases the stability of the complex. J. L. PROSSER

3609. **Relationships between metal-complex stability and the structure of the complexing agents.** G. Schwarzenbach (Eidg. Tech. Hochsch., Zürich). *Anal. Chem.* 1960, **32** (1), 6–9.—The range of complexing agents is sub-divided into unidentate, bridging and chelating ligands, and into general and selective complexing agents. The principles governing the selection of complexing agents for specific problems are discussed, and an example is given of the modification in properties of a chelating agent in the series ethylenediaminebis(acetylacetone), *cis*- and *trans*-1:2-diamino*cyclo*hexanebis(acetylacetone). T. R. ANDREW

3610. **Comparison of the alkali[-metal] methoxides in the high-frequency titration of acids in dimethylformamide.** S. F. Ting, W. S. Jeffery and E. L. Grove (State Univ., University, Ala., U.S.A.). *Talanta*, 1960, **3** (3), 240–248 (in English).—The strengths of the five alkali-metal methoxides, dissolved in benzene-methonol (9:1), were compared by h.f. response and conductance curves and by titration of some organic acids (including benzoic, salicylic, dichloroacetic and *o*-nitrobenzoic acids) dissolved in dimethylformamide (**I**). The methoxides of Cs and Rb are the strongest, but their basicity is not sufficiently different from that of the methoxides of K and Na to justify their preferred use. Lithium methoxide acts as a very weak base, but slowly dissociates with increasing concn. of methanol in the solvent. There is evidence for slight reaction of CH_3O^- with **I**. Salicylic acid behaves as a weak acid in impure **I**, but as a moderately strong acid in pure **I**. The end-points of the instrumental titrations conformed with the theoretical amount of acid when the strong methoxides were used as the titrant, and also with the thymol blue end-points for those acids having pK_a values > 3. The high-frequency method is more convenient than is the conductimetric method, mainly because of the greater ease of handling the cells in an inert atmosphere. W. J. BAKER

3611. **New cryoscopic micro-method for the determination of molecular weights.** W. H. Smit, J. H. Ruyter and H. F. van Wijk (Fysisch Chem. Inst. T.N.O., Utrecht, Netherlands). *Anal. Chim. Acta*, 1960, **22** (1), 8–16 (in English).—The method is based on temp.-heat content curves and is applicable even when solute and solvent form mixed crystals. About 2 mg of the substance is required and the accuracy is better than 1%. H. N. S.

See also Abstracts—**3687**, Molar extinction coeff. of dithizone and Pb dithizonate. **3688**, Extraction constant of Pb dithizonate. **3746**, Use of xylenol orange. **3763**, Use of the 2:4-dinitrophenylhydrazone of diacetyl monoxime as a reagent for Co. **3876**, Use of 5-hydroxy-1-tetralone for blood sugar.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

3612. **Luminescence spectra from high-frequency excitation. I. The spectra of some inorganic gases.** T. Given, R. J. Magee and C. L. Wilson (Dept. of Chem., The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1959, **3** (2), 191–199 (in English).—The construction of a high-frequency (Tesla) excitation cell and a generator producing sinusoidal current of 200 kc/s at 5 to 15 kV is described. Luminescence spectra of air, O, CO_2, N and Ar have been recorded with this apparatus in combination with a u.v. spectrophotometer. G. BURGER

3613. **Microchemical method for the detection of some elements based on the formation of luminescent products.** K. P. Stolyarov and N. N. Grigor'ev. *Vestn. Leningr. Univ.*, 1959, No. 22, *Ser. Fiz. i Khim.*, (4), 104–111.—A method for the detection of 16 elements in amounts of 1 to 10 μg in a sample of $\simeq$ 5 mg is suggested. The method is based on the formation of substances that will luminesce under u.v. light, either by the preparation of "phosphocrystals" by the introduction of micro quantities of the elements into crystals of various compounds [*e.g.*, CaO, KI or $K_4Fe(CN)_6$] or by the natural luminescence of compounds formed by chemical reaction. The method was tested on samples containing small amounts (0·1 to 0·2%) of Bi, Cd, Ni, Co, Zn, In, Ga, Hg, Sn, Sb, As, Tl, Pb and Mn in the

presence of large amounts (99·8 to 99·9%) of Fe and Cu; Fe and Cu kill the luminescence, and were therefore removed, Fe by extraction with diethyl ether and Cu by electrolysis with a mercury cathode at 0·05 V. Full details of the technique are given and reactions for the detection of Ag, Tl, As, Sb, Ga, In, Cd and Zn are described. The sensitivity is 0·01 to 0·0005 μg in 0·001 to 0·003 ml.

W. Roubo

3614. **Studies on di-substituted dithiocarbamates. VIII. Extractions with diethylammonium diethyldithiocarbamate solutions in organic solvents.** H. Bode and F. Neumann (Inorg. Chem. Inst., Tech. Coll., Hanover, Germany). *Z. anal. Chem.*, 1960, **172** (1), 1–21.—The behaviour is described of Cu^{II}, Ag^{I}, Au^{III}, Zn^{II}, Cd^{II}, Hg^{II}, Ga^{III}, In^{III}, Tl^{I}, Tl^{III}, Sn^{II}, Sn^{IV}, Pb^{II}, As^{III}, Sb^{III}, Bi^{III}, V^{V}, Nb^{V}, Se^{IV}, Te^{IV}, Cr^{III}, Cr^{VI}, Mo^{VI}, W^{VI}, Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Ru^{III}, Rh^{III}, Pd^{II}, Os^{IV}, Ir^{IV}, Pt^{II} and Pt^{IV} in extractions with 0·04% diethylammonium diethyldithiocarbamate soln. in CCl_4 at pH values from 1 to 12. Extraction procedures and methods of determination previously published are reviewed. (62 references.) B. B. Bauminger

3615. **Titration of metal oxinates in ethylenediamine with potassium methoxide.** E. E. Underwood and A. L. Underwood (Emory Univ., Atlanta, Ga., U.S.A.). *Talanta*, 1960, **3** (3), 249–254 (in English).—Some metal oxinates can be titrated in ethylenediamine and an inert atmosphere with 0·1 *N* K methoxide dissolved in benzene - methanol, the end-point being determined conductimetrically. With 2 to 13 mg of metal in the sample soln., the error is usually $<1\%$. Oxinates of Al, Zn, Sc, Th, Mo, W, V and Mg give sharp end-points, oxinates of U, Cu and Mn give fair to poor end-points, whilst oxinates of Ni, La, Fe and Tl give useless end-points. The oxinates probably behave as weak acids in ethylenediamine soln. W. J. Baker

3616. **Studies on controlled-potential electrolysis. VIII. Electrolytic analysis of metals with EDTA as supporting electrolyte.** Masao Tanaka (Bessi Mine Office, Niihama, Ehime-ken). *Japan Analyst*, 1959, **8** (8), 501–508.—The deposition potentials of Au, Ag, Hg, Cu, Bi, Sb, Pb, Cd, Sn, Ni, Co and Zn were measured at various pH values in EDTA soln. containing NH_4NO_3, NH_4Cl and ammonium acetate. All these metals, except Ni, Co and Zn, are deposited on the cathode, but only Cu, Cd and Ag are deposited quantitatively. The error is always positive and the deposit contains considerable amounts of EDTA. The extent to which the analytical result deviates from the expected value increases with increase in EDTA content.

IX. Analysis of copper alloys. Masao Tanaka. *Ibid.*, 1959, **8** (8), 508–513.—The electrolytic determination of Cu, Ni and Zn in high-purity copper alloys was examined in various soln. Copper in brass is determined by electrolysis in 0·45 *N* H_2SO_4 for 2 hr. at $-0{\cdot}20$ V *vs.* the S.C.E. and Zn successively in the residual electrolyte made ammoniacal [0·15 *N* aq. NH_3 containing 0·6 *M* $(NH_4)_2SO_4$] for 1·5 hr. at $-1{\cdot}40$ V. Copper in copper - nickel alloys is determined by electrolysis in an ammoniacal soln. at $-0{\cdot}60$ V for 3 hr. and Ni at $-1{\cdot}15$ V for 2 hr. K. Saito

3617. **Pulse-polarographic determination of lead, zinc, copper, thallium and indium in mineral raw materials.** B. Ya. Kaplan (Geological Dept. of the Central Regions). *Zavod. Lab.*, 1959, **25** (10), 1168–1172.—Applications of the apparatus previously described (Kaplan, *Ibid.*, 1957, **23**, 771; Kaplan and Ulanovskiĭ, *Ibid.*, 1958, **24**, 1414) are described.

G. S. Smith

3618. **Chel[at]ometric methods in rapid applied analysis. III. Analysis of low-melting bismuth - lead - cadmium - tin alloys.** R. Přibil and M. Kopanica (Chem. Inst., Acad. of Sci., Prague, Czechoslovakia). *Chemist Analyst*, 1959, **48** (4), 87–90.—The analysis of low-temp. alloys by EDTA titration is described in detail. Bismuth can be titrated directly at pH 1 to 2, with xylenol orange as indicator; Pb and Cd can then be titrated in the same aliquot after adjustment of the pH to between 5 and 6 with hexamine. Differentiation of these two metals may be accomplished by decomposing the Cd - EDTA complex with 1:10-phenanthroline and titrating the EDTA so released with $Pb(NO_3)_2$ soln. Tin must be removed before the titration of the other metals, either by volatilising with HNO_3 - HBr or, if it is necessary to determine Sn, by pptn. as metastannic acid. In this last procedure it is necessary to wash heavy metals out of the ppt. carefully with ammoniacal EDTA soln.

G. S. Roberts

3619. **Application of the method of "separate exposures" to the analysis of certain alloys.** E. P. Barankina. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1959, **23** (9), 1145–1147; *Ref. Zhur., Khim.*, 1960, (6), Abstr. No. 22,107.—The methods used to analyse steel, aluminium and magnesium alloys have been described previously (Andersson *et al.*, *Acta Chem. Scand.*, 1958, **12**, 415). The difference between the results of chemical and spectrographic (spark-excitation) methods in determining Si in steel is 2·5%. An additional exposure of the iron spectrum to obtain a comparison line is carried out with Armco iron electrodes. The determination of Al, Zn, Mn and Be in magnesium alloy is also carried out by the spark-excitation method with an additional exposure of the spectrum, with pure magnesium electrodes. The calibration curves are linear. The difference between the results of the chemical and spectrographic methods is 3% for Al, and 5% for Zn and Mn. The Be concn. was found to be in the range of 2×10^{-4} to 2×10^{-3} %. The calibration curve of $\triangle S$ *vs.* log *C* for Be is non-linear. The method of "separate exposures" is used in the absence of a set of standards. K. R. C.

3620. **Some separations of radio-isotopes by means of ethylenediaminetetra-acetic acid.** G. Duyckaerts and R. Lejeune (Lab. de Chim. Anal., Univ. de Liège, Belgium). *J. Chromatography*, 1960, **3** (1), 58–62 (in French).—By using a column of Dowex 50 (ammonium form), with 0·01 *M* EDTA buffered to a suitable pH as eluent, the following mixtures were separated—^{90}Y, ^{140}La, ^{90}Sr and ^{140}Ba; ^{228}Ac, ^{212}Bi, ^{212}Pb and ^{228}Ra; and ^{45}Ca, ^{90}Sr, ^{140}Ba and ^{226}Ra. W. T. Carter

3621. **Spectrophotometric detection of the end-point in the Karl Fischer titration of water.** K. A. Connors and Takeru Higuchi (Sch. of Pharm., Univ. of Wisconsin, Madison, U.S.A.). *Chemist Analyst*, 1959, **48** (4), 91–92.—A reproducibility of $\simeq 0{\cdot}0003\%$ of H_2O in methanol was obtained in Fischer titrations when the end-point was detected spectrophotometrically at 525 mμ.

G. S. Roberts

3622. **Determination of impurities in helium by gas chromatography.** A. W. Mosen and G. Buzzelli (John Jay Hopkins Lab. for Pure and Appl. Sci., General Dynamics Corp., San Diego, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 141–142.—In the method described, a charcoal trap cooled with liquid nitrogen is used to concentrate the impurities, and a Type 5A Linde Molecular Sieve column 100 cm long is used, at 50°, for the separation of H, O, N, methane and CO. A silica-gel column at 70° is used to determine CO_2. Because of peak-inversion effects and low instrumental sensitivity, H cannot be determined accurately. The other impurities can be determined at concn. from < 1 p.p.m. up to about 0·1%. K. A. PROCTOR

3623. **Use of zeolites in gas chromatography. II. Determination of argon in the presence of oxygen and other inert gases.** M. Krejčí and J. Janák (Gas Analysis Lab., Acad. Sci., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 3887–3892 (in German).—Oxygen can be removed from the mixture of gases by means of palladium finely dispersed on Alusil, with hydrogen as the carrier gas. The properties of calcium zeolite ($CaO.Al_2O_3.2SiO_2$) can be used for the separation of argon from other gases. Suitable conditions (temp., rate of flow) were found and used for a rapid routine control of the argon content of gases during air-fractionation, during NH_3 synthesis, hydrogen production, etc. The calcium zeolite (grain size 0·2 to 0·4 mm) was previously heated for 4 hr. at 400°; a similar activation of Alusil (*cf.* Janák, *Anal. Abstr.*, 1955, **2**, 1450) was carried out for 3 hr. J. ZÝKA

3624. **Conductimetric determination of alkali metals and ammonium in the presence of magnesium.** V. Novák (Dept. Anal. Chem., Inst. Chem. Technology, Pardubice, Czechoslovakia). *Sb. Věd. Prac., Vysoké Školy Chem.-Technol., Pardubice*, 1959, 121–138.—A literature survey is presented and a new method is described which consists in the conversion of the chlorides of Li, Na, K and NH_4^+ into hydroxides by means of Ag_2O and their conductimetric titration in ethanolic soln. with an ethanolic soln. of $HClO_4$ or with H_3PO_4 soln. Sodium, K and NH_4^+ can be differentiated, and K determined in the presence of an excess of Na, Li and NH_4^+ by titration with $HClO_4$ soln.; Li can be determined in the presence of K, Na and NH_4^+ by titration with H_3PO_4 soln. (96 references.) J. ZÝKA

3625. **Analysis of lithium metal, hydride and hydroxide for nickel, copper, silicon, iron, chromium, aluminium and hydroxide.** H. A. Friedman (Oak Ridge Nat. Lab., Oak Ridge, Tenn.). *Anal. Chem.*, 1960, **32** (1), 137.—A review of suitable procedures is given. (15 references.) T. R. ANDREW

3626. **Separation of potassium, sodium, calcium and magnesium ions by paper chromatography.** A. E. Petrov-Spiridonov. *Izv. Timiryazevsk. Sel.-Khoz. Akad.*, 1959, (1), 229–231; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4567.—The solvent used is pyridine - ethanol - 1·5 *N* acetic acid (2:2:1). To detect Na, treat the chromatogram with 2 *N* acetic acid, dry, spray with a soln. of zinc uranyl acetate, set aside for 3 or 4 hr. and examine in u.v. light; Na appears as a sky-blue fluorescent spot on a lilac background. Potassium is detected with a soln. of $NaPb[Co(NO_2)_6]$ (dark grey - green spots on an orange background). To detect Ca and Mg, treat the chromatogram first with a 0·5% soln. of 8-hydroxyquinoline and then with NH_3 vapour, dry at room temp. and examine in u.v. light; Ca appears as a white and Mg as a yellow - green fluorescent spot on a violet background. The method may be used for determining Na, K, Ca and Mg in biological materials; in this case the chromatogram is cut and eluted with water (3 ml) for 3 hr. Sodium and K are determined polarographically and Ca and Mg colorimetrically. C. D. KOPKIN

3627. **Colorimetric determination of potassium with dilituric acid.** R. Palouš, V. Pavelka and M. Mára (Inst. Chem., Pedagog. School, Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 3910–3914 (in German).—Yellow soln. of dilituric acid (5-nitrobarbituric acid) (**I**) are decolorised stoicheiometrically by K^+, which form a difficultly sol. ppt. with **I** in neutral or acid soln. The extinction of the separated yellow soln. is measured. *Procedure*—To 0·034 *N* **I** (5 ml) add 0·1 to 0·01 *N* KCl (2 ml), mix, set aside for 12 hr., separate the ppt. by centrifuging or filtration, and measure the extinction of the filtrate at 420 mμ. The method can be carried out in the presence of Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ or PO_4^{3-}, in *N* soln. of the salts of Li, Na or Al; NH_4^+, Sn^{II}, Fe^{II}, Fe^{III}, Cr, Cd, Cu, Mn, Ca, Ba, Zn, Co, Ni, Sr, Hg^I, Ag, Pb and coloured anions $[CrO_4^{2-}$, MnO_4^-, $Fe(CN)_6^{3-}]$ interfere. J. ZÝKA

3628. **Analytical use of 8-mercaptoquinoline (thiooxine) and its derivatives. XII. Composition and structure of copper thio-oxinate.** Yu. A. Bankovskiĭ, A. F. Ievin'sh and E. A. Luksha. *Izv. Akad. Nauk Latv. SSR*, 1959, (4), 61–68; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4314.—8-Mercaptoquinoline reacts with Cu^+ and Cu^{2+} to form $Cu(C_9H_6NS)$-C_9H_7NS, in which Cu^+ has the co-ordination number 4. The molar extinction coeff. of the complex is 9550 at the wavelength of max. absorption (432 mμ).

XIII. New specific reaction for copper with thiooxine disulphide [8:8′-diquinolyl disulphide]. Yu. A. Bankovskiĭ, A. F. Ievin'sh, Z. E. Liepinya, E. A. Luksha and L. M. Rengart. *Ibid.*, 1959, (5), 91–98; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4588.—The reaction is based on the reduction of Cu^{2+} with 8:8′-diquinolyl disulphide with the formation of $Cu(C_9H_6NS).C_9H_7NS$. The main advantage of this reaction is the possibility of detecting microgram amounts of Cu in the presence of large amounts of accompanying elements; it may be used for detecting traces of Cu in metals, alloys, salts, minerals, etc. Only Au interferes. The reason for the high specificity of this reaction is the equimolar proportion of reagent and Cu in the complex. C. D. KOPKIN

3629. **Amperometric determination of copper with salicylamidoxime.** D. Banerjea and B. Chakravarty (Indian Ass. for the Cultivation of Sci., Jadavpur, Calcutta). *J. Indian Chem. Soc.*, 1960, **37** (1), 43–44.—Take an aliquot of soln., containing 0·4 to 8 mg of Cu^{II}, adjust to pH 6 to 7 with dil. KOH soln. and add 30 ml of acetate buffer (16·5 g of Na acetate and 25 ml of glacial acetic acid diluted to 1 litre) for every 100 ml of soln. Add about 0·01 g of gelatin and dilute to a known vol. Transfer an aliquot to the titration cell and de-aerate with N. Titrate with an aq. soln. of salicylamidoxime (at least 10 times the molar concn. of the Cu soln.) at

−0·2 V against a S.C.E. A pen-recording polarograph was used with a titration cell connected to an external S.C.E. through an agar - KCl bridge. A manual circuit was employed with a micro-ammeter (0 to 50 μA) for measuring the current. A dropping-mercury electrode of drop-time $\simeq$ 3 sec. was used as indicator electrode. Lead, Cd, Zn, Mn, Co, Ni, Cl^-, NO_3^- and SO_4^{2-} do not interfere; Ag, Sb and Bi must be removed by pptn. with KCl.

G. S. ROBERTS

3630. **Determination of copper by αβ-dioximinoacetoacetanilide [αβ-dioximinobutyranilide].** J. S. Dave and A. M. Talati (Textile Chem. Dept., M.S. Univ., Baroda, India). *J. Indian Chem. Soc.*, 1959, **36** (12), 830–832.—Copper (7 to 20 mg in 200 ml of soln.) is pptd. quant. at $\simeq$ 60° and pH 6 to 7 by the addition of an excess of αβ-dioximinobutyranilide (1% ethanolic soln.). After digestion on a water bath for $\simeq$ 30 min., the ppt. is collected, washed with H_2O, and dried to constant wt. (as $CuC_{20}H_{20}O_4N_8$) at 110° to 120°. Calcium, Sr, Ba, Mg, Zn, Cd, Br^-, I^-, SO_4^{2-} and NO_3^- do not interfere. The error is usually from −0·01 to −0·09 mg.

W. J. BAKER

3631. **Arsenometric determination of cuprous and cupric ions in the presence of each other.** S. A. Kiss (Chem. Combine, Borsod, Hungary). *Magyar Kém. Lapja*, 1959, **14** (12), 497–499.—Iodine oxidises Cu^I to Cu^{II}; the reverse reaction is prevented by complexing the Cu^{II} with tartrate. From the amount of iodine used for the oxidation, the Cu^I concn. is calculated. In acid soln. the complex decomposes and the liberated Cu^{II} converts I^- into iodine. *Procedure*—Into a flask containing 0·1 *N* iodine soln. (10 ml) and *M* K Na tartrate soln. (10 ml) measure the sample (10 ml, containing 5 to 40 mg of Cu^I) and immediately acidify slightly with H_2SO_4. Add solid $NaHCO_3$ until the evolution of CO_2 ceases and then add $\simeq$ 1 g more. Titrate the excess of iodine with 0·1 *N* As_2O_3, with starch as indicator. The concn. of Cu^I is calculated from the amount of iodine consumed. Acidify the titrated soln. with H_2SO_4 (20%) and add 5 ml of a soln. containing KI (6 g per litre) and KSCN (50 g per litre). The liberated iodine (which is equiv. to the total Cu content) is titrated with 0·1 *N* $Na_2S_2O_3$. When the Cu^I content is 1 to 5 mg, use only 5 ml of 0·1 *N* iodine, and, when the Cu^I content is 0·05 to 1 mg, use 0·01 *N* iodine and 0·01 *N* As_2O_3. Formate, CO_3^{2-}, NH_4^+ and the complex of Cu tetra-ammino-formate with CO do not interfere. A. G. PETO

3632. **Photometric determination of copper in aluminium and steel with diethyldithiocarbamate.** A. S. Andreev and S. Kaĭn. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 42–45; *Ref. Zhur., Khim.*, 1960, (1), Abstr. No. 844.—Tervalent iron is masked with citric acid (**I**) at pH 9 to 9·5, and Ni is removed by extraction as the dimethylglyoxime (**II**) complex or masked with EDTA (disodium salt) (**III**). *Procedure for aluminium*—Dissolve the sample ($\simeq$ 1 g) in a mixture of HCl, H_2SO_4 and HNO_3, evaporate to fumes of SO_3, add about 100 ml of water, heat and filter. Add to the filtrate 5 to 10 ml of 20% **I** soln., neutralise to litmus with aq. NH_3, add 0·5 ml of a 1% ethanolic soln. of **II** and extract with CCl_4 (3 × 3 ml). Wash the extract with 5 ml of aq. NH_3 (1:50) and add the wash soln. to the main soln. (Instead of **II**, 20% **I** soln. and 10% **III** soln. may be used.) To this add 1 ml of a 0·1% soln. of Na diethyldithiocarbamate (**IV**) and extract with CCl_4 (5 × 5 ml), shaking for 2 min. each time. Filter the combined extracts through a filter-paper moistened with CCl_4 and measure the extinction with a blue filter (max. transmission at $\simeq$ 450 mμ) in 20-mm cells. The determination takes 2·5 hr. *Procedure for Cu in steel*—Dissolve the sample (0·25 to 0·50 g) in HCl, add HNO_3, boil to remove oxides of N and make up to 500 ml. To 10 or 20 ml of the resulting soln. add 5 ml of 20% **I** soln. and 10% **III** soln., neutralise with aq. NH_3, add **IV** and continue as described above. The absolute error in determining $\simeq$ 0·0005% of Cu is $\pm$0·00002%; the determination takes 30 min. C. D. KOPKIN

3633. **Estimation of copper and nickel by αβ-dioximinoacetoacet-o-chloroanilide [αβ-dioximinobutyro-o-chloroanilide].** J. S. Dave and A. M. Talati (M.S. Univ., Baroda, India). *J. Indian Chem. Soc.*, 1960, **37** (1), 40–42.—Further study of the method described previously (*Anal. Abstr.*, 1960, **7**, 1376, 3268, 3771) is reported. It has been shown that Cu is completely pptd. between pH 2·1 and 8·9, and Ni between pH 4·4 and 9·4. The effect of the addition of a variety of common ions has been found to be negligible. G. S. ROBERTS

3634. **A new rapid gravimetric method for the determination of silver.** E. Popper, L. Popa, V. Junie and L. Roman. *Rev. Chim., Bucharest*, 1960, **11** (1), 44–46.—A new reagent, 2-anilino-5-mercapto-1:3:4-thiadiazole (**I**) is used. A 1% ethanolic soln. is used for ethanolic soln. of Ag salts; the ppt. (from a hot soln.) is weighed. For aq. soln. of Ag salts an aq. soln. of the Na salt of **I** is used. The sensitivity is 8 μg of Ag per ml. H. SHER

3635. **Hydrazine sulphate as volumetric reagent (hydrazinometry). VI. Determination of silver.** J. Vulterin and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 206–209 (in Russian).—In an aq. NH_3 medium containing a satisfactory amount of NaOH or KOH, Ag^+ are reduced quant. to the metallic state with hydrazine sulphate as volumetric reagent. *Procedure*—To the soln. of the sample (containing 40 to 200 mg of Ag) add aq. NH_3 (10%) dropwise till the sol. complex is formed. Then add NaOH soln. (30%) (20 ml), dilute with H_2O to 50 ml and titrate with 0·05 *M* hydrazine sulphate potentiometrically. No interference is caused by the presence of the following concn. of elements—Ag:Cu = 3:1, Ag:Zn = 1:25, Ag:Ni = 1:3, Ag:Pb = 1:5, Ag:Al = 1:2, Ag:Cd = 1:5, Ag:Fe = 1:2. J. ZÝKA

3636. **Electro-analysis by isotope dilution. I. Micro-coulometer for radioactive silver and for silver determination.** J. Růžička (Dept. Nucl. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 199–205 (in German).—A coulometer suitable for the study of electro-reactions with the use of radioactive isotopes was constructed. Its use, in conjunction with electrolysis and with the method of isotope dilution, represents a new method by means of which the weighing of the deposited metal can be omitted. A range of measurement of 0·05 to 0·80 coulomb was achieved with the use of a scintillation technique and of ^{110}Ag (specific activity 10 mC per g, current density 0·03 to 0·30 mA per sq. cm). J. ZÝKA

3637. **Analysis of silver solders by anion exchange and EDTA titration.** S. L. Jones (Materials and

Processes Lab., Large Steam Turbine-Generator Dept., General Electric Co., Schenectady, U.S.A.). *Anal. Chim. Acta*, 1959, **21** (6), 532–536 (in English).—Alloys of Ag with Ni, Cu, Zn and Cd are analysed by dissolution in 8 *M* HNO_3, potentiometric titration of Ag with HCl (0·1 *N*), separation of AgCl, adjustment of the HCl concn. to 6 *N* and passage of the soln. through an anion-exchange resin. The metals, as their chloro complexes, are eluted by washing the resin with decreasing concn. of HCl (for Ni, 6 *N*; Cu, *N*; Zn, 0·01 *N*; and Cd, H_2O) and the eluates are made ammoniacal and titrated with EDTA. T. R. ANDREW

3638. **Flame-photometric determination of the alkaline-earth metals.** E. Pungor and A. J. Hegedüs (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1960, (1), 87–101 (in German).—The behaviour of mixtures of Ca, Sr and Ba is discussed, with special reference to the analysis of oxide cathodes, and methods for correcting for additive interference are given. The mechanism of thermal dissociation is outlined and detailed results are given to illustrate the effect of mineral acids, alkalis and alcohols on the emission of Ca. W. T. CARTER

3639. **Separation of minute amounts of beryllium on silica gel. (Preliminary communication.)** Z. Šulcek, J. Michal and J. Doležal (Centr. Geol. Inst., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 283–284.—From soln. of pH 4·5 to 9·5, micro amounts of Be can be retained in the form of colloidal hydroxide or hydroxo complex on a column of silica gel, then quant. eluted with dil. HCl and determined by a suitable method. Even 10^{-7} *M* soln. of Be salts can be thus separated. The adsorption on the silica gel can be carried out also in the presence of EDTA and so the quant. separation of Be in a 12,000-fold excess of Fe^{3+}, Al^{3+}, Mg^{2+}, Mn^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and VO^{2+} is possible. Phosphates, fluorides (at pH $\gtrsim$ 7) and Ti ($\gtrsim$ 100-fold excess), oxalates and tartrates do not interfere. Preparation of the silica gel used is described in a previous communication (*Coll. Czech. Chem. Commun.*, 1959, **24**, 1815). J. ZÝKA

3640. **Electrometric non-compensated method of titration of beryllium.** V. F. Barkovskiĭ (A. M. Gorki Ural State Univ.). *Zavod. Lab.*, 1959, **25** (10), 1175–1177.—The titration of a soln. of Be in the presence of an acetate buffer and NaCl is carried out with a soln. of NH_4F, which gives BeF_2. The indicator electrode is aluminium and the reference electrode is nichrome. No interference is caused by Mg^{2+}, NO_3^-, SO_4^{2-}, oxalate, and small amounts of Ca and Ba. The interference of large amounts of Ca and Ba can be prevented by the addition of EDTA. The interference of Fe^{III} is prevented by reduction with zinc or ascorbic acid, and that of Al by the addition of oxalic acid. To determine Be and Al when present together, one portion of the soln. is used for the determination of the sum of both metals, and a second, to which oxalate has been added, is used for the separate titration of Be. To determine Be in bronze, the sample (0·2 g) is dissolved in 5 ml of dil. HNO_3 (1:1) and the soln. is evaporated twice with 5 ml of conc. HCl. After dilution to between 10 and 15 ml the soln. is heated with a few pieces of granulated zinc to precipitate the Cu and reduce the Fe^{3+}. The filtered soln. is mixed with 10 ml of 20% NaCl soln., 10 ml of 20% ammonium acetate soln. and 0·5 ml of 0·1% bromophenol blue soln., the pH is adjusted to between 3·8 and 5, and titration is carried out with 0·1 *M* NH_4F. G. S. SMITH

3641. **Cation-exchange elution of magnesium ions by hydrochloric and perchloric acids.** C. K. Mann (Dept. of Chem., Florida State Univ., Tallahassee, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 67–70.—The elution of Mg^{2+} from Dowex-50W resin with various degrees of cross-linkage has been studied for several concn. of HCl and $HClO_4$. The effect of flow-rate is also reported for HCl (*M* and 10 *M*). T. R. ANDREW

3642. **Determination of calcium and magnesium with (ethylenedinitrilo)tetra-acetic acid. Studies in accuracy.** L. L. Lewis and L. M. Melnick (Appl. Res. Lab., U.S. Steel Corp., Monroeville, Pa.). *Anal. Chem.*, 1960, **32** (1), 38–42.—By the use of carefully prepared and purified reagents the correct colour end-point for the titration of Ca^{2+} with EDTA (disodium salt) soln. at pH 12·5 was determined for the indicators Calcon (C.I. Mordant Black 17) and Cal-Red [3-hydroxy-4-(2-hydroxy-4-sulpho-1-naphthylazo)-2-naphthoic acid]. For both indicators the true end-point was shown to be blue-green rather than blue, titration to the blue end-point giving results low by about 0·4%. In the presence of Mg^{2+}, however, it is advocated that 95% of the required EDTA (disodium salt) be added before adjustment of the pH to 12·5, followed by addition of the buffer soln., stirring for 2 min. and, after addition of indicator, rapidly titrating to the first (non-permanent) pure blue colour, with EDTA (disodium salt) soln. Recoveries of 6 to 24 mg of Ca in the presence of 0 to 24 mg of Mg show errors from −0·05 to +0·06 mg. Results on two NBS standard samples (Dolomite No. 88 and Limestone No. 1a) suggest that the certificated values for Ca are high. T. R. ANDREW

3643. **Rapid paper-chromatographic determination of barium, calcium, strontium and magnesium.** G. de Vries, M. J. Hardonk and K. H. J. Buschow (Chem. Lab., Vrije Univ., Amsterdam, Netherlands). *Anal. Chim. Acta*, 1959, **21** (6), 568–571 (in German).—A procedure is described for the radial paper chromatography of Ba, Ca, Sr and Mg, with a mixture of HCl (8 *N*), methanol and tetrahydrofuran (7:2:1, by vol.) as developer. After full development of the paper it is treated with 8-hydroxyquinoline, dried, and exposed to NH_3 fumes, and examined under u.v. irradiation. As little as 1 μg of one ion may be detected in the presence of up to 100 μg of another. T. R. ANDREW

3644. **Flame-photometric determination of small amounts of strontium in the presence of much calcium and barium.** E. Pungor and I. Konkoly-Thege (Inst. Inorg. and Anal. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1959, **65** (12), 466–468.—This is the Hungarian version of a paper published, in German, in *Mikrochim. Acta*, 1959, 712; *cf. Anal. Abstr.*, 1960, **7**, 897. A. G. PETO

3645. **Analytical method for the radiochemical determination of strontium-89 and strontium-90 in plant solutions.** U.K.A.E.A. (Industrial Group, Chem. Services Dept., Windscale, England). U.K.A.E.A. Report. PG Report 84 (W), 1960. 14 pp.—Full details are given of the procedure and

calculations. Radio-strontium is recovered from soln. in Butex or tributyl phosphate - kerosine by extraction with dil. HNO_3 and the procedure is then as for aq. soln., which involves pptn. of the Sr, together with carrier, by fuming HNO_3, scavenging with $Fe(OH)_3$ and pptn. of Sr oxalate monohydrate, which is β-counted without delay. For the determination of ^{90}Sr, either the source is re-counted after 3 days (if the ratio of ^{90}Sr to ^{89}Sr is in the range 0·2 to 5) or the grown-in ^{90}Y is separated and β-counted. Radio-barium is counted with radio-strontium, and Ca and SO_4^{2-} interfere if present in large amounts. G. J. HUNTER

3646. **Determination of zinc with zincon and the protecting action of polyphosphates in the determination of trace elements.** W. T. Binnerts (Landbouwhogeschool, Wageningen, Netherlands). *Chem. Weekbl.*, 1960, **56** (5), 66–67.—For the determination of Zn in organic material wet destruction and the use of zincon as a reagent for Zn are preferred to dry-ashing and the use of dithizone. No interference is caused by Cd, Co, Ni or Pb. It is probable that the protecting action of polyphosphates in the determination of Zn (*Anal. Abstr.*, 1960, **7**, 3647) can also be used in the determination of other trace elements. M. J. MAURICE

3647. **Method for ashing organic material without loss of zinc, and the determination of zinc with dithizone.** W. A. C. Campen and H. Dumoulin (Rijkslandbouwproefstation, Maastricht, Netherlands). *Chem. Weekbl.*, 1959, **55** (45), 632–633.—The loss of Zn by volatilisation during the ashing of organic material is avoided by dry-ashing the sample with $Ca(H_2PO_4)_2.H_2O$; this reacts with Zn to form a polymer, which, even when ashed at 900°, loses no Zn. The ash is dissolved in HCl, and Zn is determined by a modified dithizone method; EDTA is added to eliminate interference from Mn, and Ca to prevent the formation of the Zn - EDTA complex. *Procedure*—Mix 10 g of the sample with 3 to 4 g of $Ca(H_2PO_4)_2.H_2O$ and dry for 1 hr. at 140° and for 1 hr. at 400°, then ignite for 1 hr. at 600°, and continue heating up to 900° until ashing is complete. Dissolve the cooled residue in 100 ml of 3 *N* HCl, make up to 250 ml with H_2O, and filter. Dilute an aliquot (> 50 ml containing > 80 μg of Zn) to about 60 ml and adjust the pH to 1·8 with citrate buffer (173 g of citric acid and 537 ml of 10% aq. NH_3 per litre). Make up to 100 ml with H_2O and remove Cu from a 25-ml aliquot by extracting with 10, 5 and 5 ml of conc. dithizone soln. (200 mg in 500 ml of $CHCl_3$). Finally extract with 5 ml of $CHCl_3$. To 5 ml of the aq. soln. add 15 ml of citrate buffer, 1 ml of Na diethyldithiocarbamate soln. (1·25 g per litre) and 1 ml of EDTA soln. [10 ml of 0·5 *M* EDTA, 5 g of $Ca(H_2PO_4)_2.H_2O$ and 10 ml of *N* HCl made up with H_2O to 100 ml]. Extract the Zn complex with two 10-ml portions of dil. dithizone soln. (5 ml of conc. soln. diluted with 160 ml. of $CHCl_3$ before use). Wash the combined extracts with aq. Na_2S soln. (5 ml of 4% $Na_2S.9H_2O$ soln. diluted to 250 ml with H_2O before use) to eliminate the excess of dithizone, and measure the extinction of the red - violet soln. at 515 mμ against a blank. Calculate the amount of Zn by reference to a calibration graph. The citrate buffer and the dithizone soln. should be freed from metal ions. M. J. MAURICE

3648. **Isotopic analysis [of zinc] with a mass spectrometer.** Junichi Okamoto, Minoru Kakuta, Nozomu Morito, Yasuo Nakajima, Hitoshi Tsuyama and Humiko Onuki (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1959, **8** (7), 445–449.—The isotopic abundance measurement of zinc was examined with reference to the ion source. The electron impact method is the best for a small amount (< 10 mg) of electromagnetically concentrated zinc. The sensitivity depends on the velocity of the electrons, 120 V being the optimum for the use of the $ZnCl^+$ peak. K. SAITO

3649. **Precipitation of zinc sulphide from acid solutions by thioacetamide.** D. F. Bowersox, D. M. Smith and E. H. Swift (Inst. of Technol., Pasadena, Calif., U.S.A.). *Talanta*, 1960, **3** (3), 282–295.—The kinetics of the pptn. of ZnS (0·01 to 0·04 *M* Zn) by 0·1 to 0·4 *M* thioacetamide (**I**) at 90° and different pH values is examined in respect of the use of **I** for the quant. pptn. of Zn or its separation from other elements, especially between pH 2 and 3. At pH < 2·5 the reaction is controlled by the rate of hydrolysis of **I** to H_2S, but from pH 4·5 to 6·5 pptn. is by direct reaction, a rate equation for which is given. In the separation of Pb (≃ 100 mg) as PbS from Zn (50 to 200 mg) in approx. 0·3 *M* HCl the use of **I** results in the co-pptn. of more Zn (≃ 0·6%), by the direct reaction, than when H_2S is used, but by modification of procedure and correct control of time and concn. of H^+ an effective separation can be made with **I**. Similarly, more Ni^{II} is co-pptd. with ZnS at approx. pH 2 when **I** is used. There is no evidence for the formation of Zn - thioacetamide complexes in neutral soln. (*Cf.* Swift, *Anal. Abstr.*, 1956, **3**, 2061; Bowersox *et al.*, *Ibid.*, 1958, **5**, 4017; 1959, **6**, 4788.)
W. J. BAKER

3650. **Radiometric titration of zinc and copper with EDTA.** I. Galateanu, I. Maxim and T. Braun (Inst. Fiz. Atom., Bucureşti, Romania). *Z. anal. Chem.*, 1960, **172** (4), 274–279 (in English).—The method previously described (Braun *et al.*, *Anal. Abstr.*, 1959, **6**, 3351) has been further studied. At the optimum pH (9 to 11·5) for the use of $^{110}AgIO_3$ (**I**) as heterogeneous indicator, Cu and Zn are pptd. as hydroxides, and two procedures are described to overcome this difficulty. In the first, a suspension of **I** of known activity is adjusted to pH 2 to 3, and the test soln. is added, followed by a slight excess of standard EDTA (disodium salt) soln. (**II**). The pH is then slowly brought to 10, and the titration is continued to give the indicator titration curve of activity *vs.* vol. of titrant, as previously described (*loc. cit.*). In the second procedure, a suspension of **I** is titrated at pH 10 with **II**, and the titration curve is plotted. The pH is then adjusted to 2 to 3 with HNO_3, the test soln. is added, and the pH is slowly raised to 10, with continuous stirring. The activity of the soln. then rises to a point lower than the original one, the difference being a measure of the vol. of **II** required to complex the Cu or Zn. When Cu and Zn are present together, the sum of the two metals is first obtained; Cu is then removed from a second aliquot of the test soln. by means of iron powder (Budevskiĭ, *Anal. Abstr.*, 1959, **6**, 842). The elementary Cu is then filtered off and dissolved in HNO_3, and the Cu is then titrated in the soln., Zn being obtained by difference. J. P. STERN

3651. **Determination of cadmium in zinc concentrates and other zinc-rich materials.** S. Kallmann, H. Oberthin and R. Liu (Res. Div., Ledoux & Co., Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1960,

32 (1), 58–60.—Zinc is quant. retained on a cation-exchange column (Amberlite 120 or Dowex 50) from soln. $< 0{\cdot}1\ N$ in HI, while Cd is not retained in the range $0{\cdot}008\ N$ to $2\ N$ in HI. This has been applied to the separation of Cd from Zn in a soln. $0{\cdot}3\ N$ in HI and $0{\cdot}15\ N$ in H_2SO_4. Cadmium (0·002 to 20%) is subsequently determined by any conventional method. T. R. ANDREW

3652. **Determination of cadmium in chromium - nickel alloys.** V. P. Razumova and L. S. Nadezhina. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 158–162; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4612.—The possible use of the method of Mahr and Ohle (*Z. anal. Chem.*, 1937, **109**, 1) for determining Cd in ferro-alloys and chromium - nickel alloys is studied. The method depends on the formation by Cd^{2+} of a practically insoluble compound of high molecular weight with thiourea (**I**) and Reinecke's salt (**II**). To determine Cd in chromium - nickel alloys, dissolve the sample in H_2SO_4, add conc. HNO_3, evaporate to fumes of SO_3 and dissolve the residue in water. Cool the soln. (60 or 70 ml) to 15° to 17°, add 5% **I** soln. and 1% **II** soln. to precipitate Cd, set aside for 1 hr. and filter. Wash the ppt. first with a soln. containing 1% each of **I** and **II** and then with a small vol. of 5% **I** soln., and dissolve it in hot water. Evaporate the soln. to a small vol., add HNO_3 to destroy the complex, add H_2SO_4, evaporate to fumes, filter off sulphur and determine Cd^{2+} in the filtrate polarographically. It is shown that the pptn. of Cd^{2+} from soln. of pure salts is quantitative at $< 18°$. The solubility of the complex in the range 0° to 100° has been determined. The relative error in determining 0·10 mg of Cd in 80 to 100 ml of a soln. of a pure salt is $\geq 10\%$; the sensitivity of the method is 0·1 mg of Cd in 100 ml of soln.
C. D. KOPKIN

3653. **Polarographic estimation of cadmium in presence of nickel, cobalt and bismuth.** H. C. Saraswat (Christ Church Coll., Kanpur, India). *Proc. Indian Acad. Sci., A*, 1960, **51** (1), 34–40.—Cadmium (10 to 40 mM) can be determined by amperometric titration with standard $K_4Fe(CN)_6$ soln. at $-1{\cdot}8$ V with the dropping-mercury electrode and the S.C.E. The precision of the method is $\pm 0{\cdot}5\%$ and interference from Ni^{2+}, Co^{2+} and Bi^{3+} can be eliminated by using $0{\cdot}5\ M$ K citrate as supporting electrolyte. W. T. CARTER

3654. **Spectrographic analysis of high-purity mercury.** A. M. Gorbacheva and E. L. Grinzald. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 77–83; *Ref. Zhur., Khim.*, 1960, (1), Abstr. No. 881.—Place the sample (10 g $\pm 0{\cdot}1$ g) in a porcelain crucible and evaporate at 350° on an electric hot-plate fixed in a glass flask into which technical oxygen is introduced; after 30 or 40 sec., at the end of the evaporation, raise the temp. to 400°. Dissolve the residue in a mixture (2:1) of dil. HNO_3 (1:1) and 3% KNO_3 soln. Place one drop of the resulting soln. on the end of a carbon lower electrode. Photograph the spectra in a medium quartz spectrograph on "spectral" plates, type I, with excitation in an a.c. arc at 3·5 amp. The electrodes are first ignited for 5 sec. and the soln. is then added to the partially cooled electrode. The analysis is carried out with a 15-μ slit, with an arc gap of 2 mm and an exposure of 20 sec. Calibration curves are constructed of S *vs.* log C from the lines (in A): Zn 3282, Ag 3280, Cd 3261, Cu 3247, Sn 3175, Bi 3067 and Pb 2833. Synthetic standards are prepared by dissolving samples of the metals in dil. HNO_3 (1:1). To remove Cu from the carbon electrodes, they are boiled for 20 min. with conc. HNO_3, washed with hot water, dried and ignited for 1 min. in an arc at 6 amp. The sensitivity of the analysis by the enrichment method is (in %): Zn, 1×10^{-4}; Ag, 4×10^{-7}; Cd, 2×10^{-5}; Cu, 1×10^{-6}; Sn, 1×10^{-5}; Bi, 2×10^{-6}; and Pb 1×10^{-5}. C. D. KOPKIN

3655. **Amperometric titration of boron with fructose.** W. B. Swann, W. M. McNabb and J. F. Hazel (Univ. of Pennsylvania, Philadelphia, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (1), 76–81 (in English).—The method is used to determine 0·1 to 2 μg of B in 25 ml of soln. The polarographic wave of fructose is depressed by BO_3^- and the magnitude of the depression provides a measure of the concn. of BO_3^-. The supporting electrolyte contains LiCl and LiOH and has a pH value of $12 \pm 0{\cdot}1$. A silver - silver chloride reference electrode is used and, with a potential of $-2{\cdot}05$ V applied to the dropping-mercury electrode, the soln. is titrated amperometrically with M fructose. Corrections are applied for dilution of sample vol. and for reagent blank, and the corrected vol. of M fructose required to produce a current increase of 1·5 μA is computed graphically. A calibration curve is constructed from the values obtained when known amounts of BO_3^- are titrated by the same procedure. H. N. S.

3656. **Determination of boron with 1:1′-dianthrimide.** L. Danielsson (Swedish Inst. for Metal Research, Stockholm). *Talanta*, 1959, **3** (2), 138–146 (in English).—The conditions for the spectrophotometric determination of B in boric acid have been studied. The boric acid is heated with H_2SO_4 and 1:1′-dianthrimide and the extinction of the soln. is measured at 620 mμ. Optimum conditions are—1:1′-dianthrimide, 0·4 mg per ml; H_2SO_4, 93 to 95% by wt.; B, 0·3 to 1·0 μg per ml; heating time 1 to 1·5 hr. at 100°, or 4·5 hr. at 80°.
G. BURGER

3657. **Indirect absorptiometric method for the determination of boron.** R. H. Campbell and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 50–54.—Optimum conditions are established for a method for the photometric determination of B based on the removal of fluoride ions from a molybdate - fluoride complex and subsequent reduction of the liberated molybdate to molybdenum blue. The interference of 28 ions is studied and it is recommended that BO_3^{3-} be separated by distillation. The soln. containing B is diluted to contain 0·1 to 2·5 mg of B per 10 ml and a 10-ml aliquot is transferred to a 250-ml polyethylene beaker. Chloroacetic acid buffer ($1{\cdot}5\ M$) (10 ml) of pH 2·2, and molybdate - fluoride soln. [$0{\cdot}1\ M$ sodium molybdate - $0{\cdot}2\ M$ KF (1:2)] (6 ml) are added, the soln. is diluted to 48 ml, and $SnCl_2.2H_2O$ soln. [0·5% in HCl (1:50)] (2 ml) is added. The soln. is allowed to stand for 40 min. and the extinction is read at 750 mμ against water.
T. R. ANDREW

3658. **Quantitative spectrographic determination of boron in seam welds and wear-resistant coatings.** A. S. Dem'yanchuk and O. P. Ryabushko. *Avtomat. Svarka*, 1959, (6), 89–90; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4678.—Standards are prepared by powder metallurgy by the hot pressing of briquettes in a protective medium. In determining 0·2 to

4·0% of B in cast iron or stainless steel the spectra are excited in an a.c. arc at 3 amp. from generator DG-1; the current strength in the primary transformer winding is 0·3 amp.; the activator discharge gap is 0·5 mm; an auxiliary carbon electrode 10 mm in diam., sharpened to a truncated cone, is used. The spectra are photographed in a medium spectrograph with slit width of 15 μ and analytical gap 2 mm without a condenser or preliminary ignition. Calibration curves are constructed from the lines B 2496·7 A and Fe 2474·8 A. A brief description is given of the use of a high-voltage condensed-spark discharge. Boron may also be determined in nickel-chromium steel by this method. C. D. KOPKIN

3659. **Volatility of boric acid from solutions and mixtures.** Sh. K. Ashratova. *Zavod. Lab.*, 1960, **26** (1), 59–60.—The boiling of neutral and acid soln. containing between 6 and 52 g of H_3BO_3 per litre results in practically no loss of H_3BO_3 in 40 min. even when a reflux condenser is not used. When 200 ml of a soln. containing 0·487 g of H_3BO_3 was evaporated to dryness on a water bath there was no loss; in the presence of 14 ml of HNO_3 the loss was between 0·007 and 0·014 g. When 1·9512 g of H_3BO_3 was dried at 130° for 2 hr. there was no loss. At 250° the loss was 0·0488 g in 2 hr.
G. S. SMITH

3660. **Volatility of boric acid.** Yu. M. Kostrikin and V. A. Korovin. *Zavod. Lab.*, 1960, **26** (1), 60–61.—That the volatility of H_3BO_3 is negligible when aq. soln. are evaporated to dryness under "normal analytical conditions" is confirmed. With extremely dil. soln., when evaporation may take some hours, it is possible to lose all the H_3BO_3. The matter is discussed theoretically.
G. S. SMITH

3661. **Determination of boron in boric acid esters.** D. L. Hunter, L. L. Petterson and H. Steinberg (U.S. Borax Research Corp., Anaheim, Calif., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (6), 523–527 (in English).—For the determination of boron in boric acid esters that are resistant to hydrolysis it is proposed to fuse the sample (0·5 to 1 g) either with Na_2CO_3 (27 g) in a platinum crucible, or with 1 g of $KClO_4$ and 15 g of Na_2O_2 in a Parr bomb, before alkalimetric titration in the presence of mannitol.
T. R. ANDREW

3662. **Complexometric determination of aluminium with dithizone as indicator.** G. Gottschalk (Osram G.m.b.H., Berlin). *Z. anal. Chem.*, 1960, **172** (3), 192–197 (in German).—The soln. in HCl or H_2SO_4, which must be free from all metals other than the alkali and alkaline-earth metals, and contain not more than 26 mg of Al, is just neutralised with 2 *N* NaOH, followed by enough 2 *N* HCl to clarify the soln. and give a slight excess. Standard EDTA (disodium salt) soln. and some Na acetate buffer soln. are added, and the soln. is heated on a water bath for 10 min. After being cooled under the tap, the soln. is diluted with an equal vol. of ethanol, and a little indicator soln. is added (0·05% dithizone in trichloroethylene). The bluish soln. is titrated with standard Zn acetate soln. until a red colour persists. The concn. of the standard soln. used depends on the amount of Al expected—0·1 *M* for 26 to 1·3 mg, 0·01 *M* for 2·6 to 0·13 mg, and 0·001 *M* for 260 to 13 μg. H. M.

3663. **Complexometric determination of aluminium.** A. A. Bashkirtseva and E. M. Yakimets (S. M. Kirov Ural Polytech. Inst.). *Zavod. Lab.*, 1959, **25** (10), 1166–1168.—To determine Al (> 50 mg) in a SiO_2-free soln. containing Fe but no elements interfering with the complexometric determination of Al, the soln. is boiled with 0·5 to 1 ml of conc. HNO_3 to oxidise Fe^{II}, and then treated with sufficient hot NaOH soln. to give a permanent ppt., and then 5 ml of *N* HCl; the soln. is then diluted to 50 ml, treated with 1 to 2 ml of 10% Na sulphosalicylate soln., and titrated with EDTA soln. to give the content of Fe. The soln. is then mixed with a measured amount of 0·05 *M* EDTA (disodium salt) sufficient to give an excess of between 2 and 10 ml over that required to combine with the Al present. The soln. is boiled and neutralised to Congo red paper with 5% aq. NH_3, and 10 ml of an acetate buffer soln. (pH 4·8) is added. In the cooled soln. the excess of EDTA is determined by titration with 0·02 *M* Fe^{3+}. Separation from interfering elements can be effected by a preliminary pptn. of Fe and Al as hydroxides.
G. S. SMITH

3664. **Quantitative determination of aluminium by the width of spectral lines.** A. Shalpȳkov. *Sb. Nauch. Rabot. Stud. Kirg. Univ.*, 1959, (2), 47–50; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4613.—In determining the photometric width of a line, the intensity of blackening in the centre of the comparison line is measured. The edge of the analytical line is then brought on to the photometer slit to obtain a blackening equal to that of the comparison line. The line reflection is then moved across the slit to obtain the same degree of blackening at the opposite edge of the line. The movement of the micrometer screw between the two edges of equal blackening is a measure of the line width. Alumina and KCl are added to carbon powder to give concn. of Al of 0·5 to 10%. The spectra are excited in an a.c. arc at 5 amp., the subtance being evaporated from a cavity in a carbon electrode. The width of the line Al 3961·5 A and the blackening of the line K 4044·1 A are measured. Calibration curves of slit width *vs.* log *C* are rectilinear over the whole concn. range, while those of $\triangle S$ *vs.* log *C* are rectilinear only up to a concn. of 2% of Al. C. D. KOPKIN

3665. **Determination of aluminium oxide in metallic aluminium.** E. I. Denisov. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 102–109; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4616.—Dissolve the sample (turnings or filings) by heating with a 20% soln. of Na tartrate, add a soln. of $(NH_4)_2SO_4.FeSO_4.6H_2O$ (0·7 g in 10 ml), heat to boiling and pass H_2S till the soln. is cool. Separate the ppt., dissolve it in 20% tartaric acid soln. and repeat the pptn. Filter and ignite the filter-paper and ppt., fuse the residue with $K_2S_2O_7$, extract the melt with 5% H_2SO_4, separate SiO_2, acidify and precipitate Cu^{2+} with H_2S. Remove the ppt., add a 3% soln. of H_2O_2 and separate Al and Fe from the K_2SO_4 by double pptn. with an excess of aq. NH_3. Dissolve the ppt. in HCl, add conc. HCl and extract with amyl acetate. Evaporate the aq. layer to dryness, dissolve the residue in HCl and make up to a known vol. In an aliquot of the resulting soln. determine Fe^{3+} iodimetrically and Al^{3+} photometrically with aluminon. In preparing the calibration curves add to each of the standard soln. the amount of Fe found as described above. It is shown that the method described gives results which agree well with those obtained by the chlorination method if a finely divided sample is used in the latter. The fineness of the sample has no effect in the tartrate method.
C. D. KOPKIN

3666. **Determination of aluminium in aluminium bronze.** N. V. Bausova. *Trudy Inst. Metallurg. Ural'sk. Filial Akad. Nauk, SSSR*, 1959, (3), 125–126; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4615.—It is shown that in the presence of EDTA (disodium salt) (**I**) NaF quant. precipitates Al from a weakly acid soln., while Cu, Fe, Co, Ni, Zn, Sn, Bi, Sb and Mn remain in soln. *Procedure*—Dissolve the sample (0·25 to 0·5 g) in 10 ml of H_2SO_4 and a few drops of HNO_3, add 30 ml of water and 30 ml of a 15% **I** soln., neutralise to methyl orange with aq. NH_3, add 0·5 ml of conc. H_2SO_4 and 40 ml of satd. NaF soln. and set aside for 20 min. Filter the ppt. through two folded filter-papers, wash it (× 5 or 6) with 0·5% NaF soln. and dissolve it in a boiling mixture of 150 ml of satd. H_3BO_3 soln., 250 ml of HCl and 600 ml of water; wash the filter (× 3) with hot water. Determine Al in the soln. gravimetrically with 8-hydroxyquinoline.

C. D. KOPKIN

3667. **Rapid determination of aluminium and fluoride in the presence of each other.** Koichi Mukai and Koichi Goto (Res. Inst., Nippon Light Metal Co., Kambara, Shizuoka-ken). *Japan Analyst*, 1959, **8** (8), 523–526.—Aluminium (< 15 mg) is pptd. quant. (> 97%) with 8-hydroxyquinoline (**I**) at pH 10 in the presence of F^- (25 to 400 mg) and determined gravimetrically by the usual method. **I** in the filtrate is removed by extraction with $CHCl_3$ (2 × 15 ml) at pH 5 to 9, and the F^- are titrated in a chloroacetate buffer of pH 3·0 with $Th(NO_3)_4$ soln., with Alizarin red S as indicator. The time taken for an estimation is ≃ 100 min. K. SAITO

3668. **Separations involving sulphides. XI. Separation of aluminium or uranium from some elements forming thio salts.** I. K. Taimni and S. N. Tandon (Chem. Lab., Univ. Allahabad, India). *Anal. Chim. Acta*, 1959, **21** (6), 502–504 (in English).—Binary mixtures of Al (≃ 10 mg) or U (≃ 60 mg) with As, Te, Sb, Se, Mo, Hg, Au, Pt or Re (≃ 50 mg) in soln. are separated by addition of excess of 2 *N* Na_2S, acidifying with HCl, boiling and, after cooling, filtering off the pptd. sulphide. The sulphide can be determined gravimetrically, and the Al or U in the filtrate can be determined as the 8-hydroxyquinoline complex. A recovery within ±0·5% is claimed. T. R. ANDREW

3669. **X-ray fluorescence spectrometric analysis. I. Analysis of copper - aluminium and silver - aluminium alloys.** Hidehiro Gotô, Shigerô Ikeda and Emiko Sudô (Inst. for Iron, Steel and Other Metals, Tohoku Univ., Katahira-cho, Sendai). *Japan Analyst*, 1959, **8** (8), 518–522.—The intensity of the $K\alpha$ and $K\beta$ fluorescence of Cu and Ag is not affected by Al under specified conditions (Machlett, AEG 50T; anti-cathode, tungsten). The ratio of the intensity of both the $K\alpha$ and $K\beta$ lines of the alloy of Cu and Ag to that of each pure metal is proportional to the wt. (%) of Cu (at 35 kV, 5 mA) and of Ag (at 50 kV, 10 mA). Results were the same for samples in powder (< 200 mesh) and in plate form. This method is applicable to the investigation of segregation of Cu in a cylindrical sample of alloy.

K. SAITO

3670. **Separation and determination of aluminium, gallium, indium and thallium by partition chromatography.** R. J. Magee and I. A. P. Scott (The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1959, **3** (2), 131–137 (in English).—These metals can be completely separated as chlorides by descending chromatography with a solvent mixture of phenol - methanol - HCl (5:3:2, w/v/v). The zones are rendered visible under u.v. light by spraying the chromatogram with a 5% soln. of 8-hydroxyquinoline in methanol - $CHCl_3$ - H_2O (12:12:1, by vol.) and exposing it to aq. NH_3 vapour. Amounts of each metal in the range 20 to 500 μg can be detected and roughly estimated by comparison with standards. Conditions for the extraction of the metal compounds and their determination in a spectrophotometer have been established. G. BURGER

3671. **Spectrophotometric determination of microgram quantities of indium in uranium and thorium metals and their salts.** V. T. Athavale, T. P. Ramachandran, M. M. Tillu and G. M. Vaidya (A.E.E. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **22** (1), 56–60 (in English).—The method deals with contents of In in the range 0·1 to 10 p.p.m. The reagents must be carefully purified before use. *Procedure*—Dissolve the sample in conc. HNO_3 and evaporate to a syrup on a water bath. Dissolve ThO_2 in conc. HNO_3 with the addition of dil. HF (1%) and remove the HF by repeated evaporation with conc. HNO_3. Dilute the syrup to 20 ml and add 10 ml of 10% ammonium citrate. Add dil. HNO_3 (1%, v/v) until the pH is 3·5 to 4 and remove Bi by extracting with 5-ml portions of dithizone (**I**) (0·02% in CCl_4) until the organic layer remains green. Wash the aq. layer with $CHCl_3$ and to it add 2 ml of 10% KCN soln. and 0·2 ml of 20% hydroxyammonium chloride soln. Adjust to pH ≃ 9 with conc. aq. NH_3 and extract with four or five 5-ml portions of 0·02% **I** soln. Wash the combined extracts with three 20-ml portions of water. Extract In, Pb and Tl from the organic layer with 20 ml of dil. HNO_3 (1%, v/v) and wash the acid extract with CCl_4. Add 13 ml of 2 *N* Na acetate and 2 ml of 20% $Na_2S_2O_3.5H_2O$ soln. and extract with 10 ml of 0·002% **I** soln., and determine the extinction of the extract at 510 mμ in a 1-cm cell in a Beckman DU spectrophotometer. Prepare a calibration graph by mixing known amounts of In in soln. with Na acetate - acetic acid buffer (pH 5 to 6), extracting with 0·002% **I** soln. and plotting the extinctions. In certain determinations the addition of various metals that form dithizonates produced no errors. H. N. S.

3672. **Determination of copper and lead in indium arsenide.** V. J. Jennings (Services Electronics Res. Lab., Baldock, Herts., England). *Analyst*, 1960, **85**, 62–68.—The weighed sample of zone-refined indium arsenide is dissolved by warming in HCl and dil. HNO_3 in a polytetrafluoroethylene beaker and the soln. is evaporated to dryness. The residue is dissolved in *M* H_3PO_4, transferred to a polarographic cell and a continuous square-wave polarogram is recorded. The determination is completed by a standard addition method in which 0·5-, 1- or 2-μg amounts of Cu and Pb as standard soln. are added to the soln. in the polarographic cell and continuous square-wave polarograms are recorded. From measurements of the peak heights of the waves due to Cu and Pb, the wt. of Cu and Pb in the sample are calculated. Concn. as low as 0·1 p.p.m. of Cu and 0·2 p.p.m. of Pb can be determined in a 0·5-g sample of indium arsenide.

A. O. JONES

3673. **Determination of thallium by ultra-violet absorption of the chloride solution.** L. B. Ginzburg

and E. P. Shkrobot (State Sci. Res. Inst. of Non-Ferrous Metals). *Zavod. Lab.*, 1959, **25** (10), 1157–1162.—In 6 *N* HCl the absorption max. of Tl is at 244 to 246 mμ, the molar extinction coeff. of $TlCl$ and $TlCl_3$ are $\simeq$ 5000 and $\simeq$ 14,000, respectively, and Beer's law is obeyed over the concn. ranges of 70 to 600 μg (for Tl^+) and 20 to 700 μg (for Tl^{3+}) in 25 ml. Since the absorption max. coincides with those of Bi, Sb, Sn, Cu, Pb and Fe in soln. of Cl^- (and also of Br^-) the separation of Tl is necessary. A method suitable for application to various non-ferrous metallurgical products is described. *Procedure*—The sample (0·5 to 1 g) is dissolved in HCl followed by HNO_3, and the soln. is evaporated two or three times with HBr containing Br. The residue is dissolved in 10 ml of *N* HBr containing Br and the filtered soln. is extracted with two equal vol. of diethyl ether satd. with *N* HBr. The extracts are washed with *N* HBr satd. with diethyl ether (2 × 5 ml), 15 ml of dil. HCl is added, ether is removed by evaporation, Br^- are removed by boiling with H_2O_2, and the excess of H_2O_2 is removed by further boiling. The cooled soln. is treated with 0·2 ml of 10% $NaNO_2$ soln. to ensure the complete oxidation of Tl^+ and, after 5 min., with 0·5 ml of 50% urea soln. The soln. is then diluted to 25 ml with dil. HCl (1 : 1) and the extinction is measured at 245 mμ. The method is suitable for determining $\lesssim$ 0·005% of Tl in a 1-g sample.

G. S. Smith

3674. **Use of mixed basal solutions in the polarographic determination of thallium.** A. I. Zebreva and M. T. Kozlovskiĭ (Kazakh State Univ.). *Zavod. Lab.*, 1959, **25** (10), 1172–1174.—Basal electrolytes containing 2 *N* NaOH and 1·5 *N* NH_4Cl, or 1·5 *N* NaOH and *N* NH_4Cl, are suitable for the polarographic determination of Tl^+ in the presence of Cd, Pb, Se, Te, As, Sb, Bi, Zn and small amounts of Fe ($\gtrsim$ 10 mg). G. S. Smith

3675. **Volumetric determination of microgram amounts of the rare-earth elements.** V. I. Kuznetsov and L. A. Okhanova (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1959, **25** (10), 1162–1165.—The method is applied to soln. containing the elements separated by chromatography or by some other procedure. The concn. should be $\lesssim$ 1 μg per ml. With 10 to 100 μg, titration is carried out in a vol. of 8 to 10 ml and, with larger amounts, in 50 to 100 ml. An aliquot of the soln. is evaporated to dryness, the residue is dissolved in 1 ml of 0·05 *N* HCl, and 1 ml (or 2 ml if the amount of rare-earth element exceeds 100 μg) of arsenazo indicator soln. is added. The indicator soln. is prepared by mixing 25 ml of 0·01% arsenazo soln. and a measured vol. of a standard soln. of the element considered to give a half-way tint (the amount required for each element is tabulated), and then diluting to 50 ml. After the addition of the indicator soln. a 10% soln. of hexamine (0·15 to 4·0 ml, in accordance with the tabulated values) is added, a comparison soln. for the end-point colour is prepared, and the soln. is titrated with a standard soln. of citric acid. In a modification, a single standard soln. of a rare-earth element is used for preparing the necessary soln. for titrating other rare-earth elements.

G. S. Smith

3676. **Study of the extraction of lanthanum complexes with benzoylacetone.** J. Starý (Dept. Nucl. Chem., Inst. Chem. Technology, Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 86–92 (in German).—In an investigation of the extraction of La with benzoylacetone (**I**) in three organic solvents ($CHCl_3$, benzene and CCl_4), the formation of a LaI_3 complex was studied and its stability constant and partition coefficient were calculated. It was found that, in a medium of pH 10 to 11, Ba cannot be extracted with 0·1 *M* soln. of **I** in benzene, whereas La is quant. extracted; a rapid method was thus developed for the separation of ^{140}La from ^{140}Ba.

J. Zýka

3677. **Determination of the partition coefficient of praseodymium and neodymium in the tributyl phosphate and nitric acid system.** A. Musil and G. Weidmann (Inst. for Inorg. and Anal. Chem., Univ. Graz, Austria). *Z. anal. Chem.*, 1960, **172** (1), 32–35.—It is shown that the partition coeff. of Pr and Nd depend on the molarity of the HNO_3 and attain their greatest values on extraction with 3 *N* acid. The measurements are carried out photometrically and the relationships between the partition coeff., the molarity of the HNO_3, and the extinctions are tabulated. B. B. Bauminger

3678. **Photometric determination of traces of carbon monoxide in hydrogen.** G. Ciuhandu and G. Krall (Inst. Hyg., Lab. Toxicol., Timişoara, Romania). *Z. anal. Chem.*, 1960, **172** (2), 81–87 (in German).—The apparatus described and illustrated is used for the determination of 0·001 to 0·5% of CO in hydrogen. The method depends on the colour that is formed when the gas is passed through an ice-cooled alkaline soln. of silver *p*-sulphamoylbenzoate and the measurement is made immediately at 420 mμ. The error is ±5% and reproducible results are obtained only when the experiments are performed under controlled conditions. B. B. Bauminger

3679. **Use of dimedone in the photometric determination of cyanides.** V. Kratochvíl (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 299–301.—The method is based on the conversion of CN^- to cyanogen chloride and its reaction with pyridine with the formation of glutaconaldehyde which reacts with dimedone (**I**). The violet colour is measured at 580 to 585 mμ. *Procedure*—Into a 50-ml flask place the soln. of the sample (containing 1 to 20 μg of CN^-), dilute with freshly boiled H_2O to about 40 ml, add chloramine T soln. (1%) (1 ml), mix and set aside for 1 min.; add the soln. of **I** (3% in 30% pyridine) (3 ml), mix and set aside for 10 min. Dilute with H_2O to vol. and after 30 to 40 min. measure the extinction. Carry out a blank and compare with a calibration curve.

J. Zýka

3680. **New analytical line of silicon.** W. J. Klimecki (Inst. Metallurgy, Gliwice, Poland). *Hilger J.*, 1960, **6** (1), 8–9.—The silicon line 2124·150 has high concentrational sensitivity and is suitable for direct-reading measurements with medium quartz spectrographs for silicon determinations in low-alloy steels. The line is not suitable for silicon determinations in aluminium and its alloys.

G. Skirrow

3681. **Determination of silicon by distillation-colorimetric method.** B. D. Holt (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 124–128.—The sample is decomposed with $HClO_4$, with the addition of HCl or HNO_3, and finally heated to fumes. After addition of HF, silicon tetrafluoride is distilled from a platinum still and

absorbed in a soln. containing ammonium molybdate and boric acid. The resulting molybdosilicate is determined photometrically at 815 mμ after reduction to molybdenum blue. From 5 to 30 μg of Si has been determined in plutonium, uranium, steel and phosphoric acid. T. R. ANDREW

3682. **Quantitative spectrochemical determination of minor elements in silicates.** Hiroshi Hamaguchi, Rokuro Kuroda and Ryokichi Negishi (Dept. of Chem., Tokyo Univ. of Educ., Japan). *Talanta*, 1959, **3** (2), 207–208 (in English).—Small amounts of Pb, Ga, Sn, Co, V, Cr and Ni in silicates can be determined by a single arcing. The powdered sample is mixed with an equal wt. of carbon powder containing Sb_2O_5 (0·8%) and Pd (0·04%) as internal standards. The mixture is packed into the crater of the lower electrode and excited for 60 sec. by an 8-amp. 210-V continuous a.c. arc. G. BURGER

3683. **Polarographic determination of germanium.** N. V. Stashkova and A. I. Zelyanskaya. *Izv. Sibirsk. Otdel., Akad. Nauk SSSR*, 1959, (1), 59–66; *Ref. Zhur., Khim.*, 1959, (23), Abstr. No. 81,943.—A study is made of the polarographic behaviour of Ge^{4+} with a dropping-mercury cathode. At pH 8, Ge^{4+} give a satisfactory polarogram ($E_{\frac{1}{2}} = -1{\cdot}41$ to $-1{\cdot}43$ V *vs.* the S.C.E.) with basal soln. consisting of 0·1 *M* Na acetate and 0·2 *M* NaCl, 0·1 *M* Na formate and 0·2 *M* NaCl, 0·07 *M* K_2SO_4 and 0·2 *M* NaCl, or 0·2 *M* NaCl, 0·04 *M* sulphanilic acid and 0·2 *M* benzoic acid. With basal soln. containing KBr, KI, K_2SO_4, NH_4SCN, Na_2CO_3, $Na_2B_4O_7$, ammonium citrate, glycerol or Na salicylate, the diffusion area is not satisfactory, but it is considerably improved by adding 0·06 to 0·3 mole of EDTA (**I**) per litre to the soln. ($E_{\frac{1}{2}} = -1{\cdot}41$ to $-1{\cdot}45$ V). With a basal soln. of $BaCl_2$, KNO_3, Na_2HPO_4, Na succinate, sulphanilic, phenylacetic or sulphosalicylic acid, the Ge wave is not satisfactory, even when **I** is present. With a mannitol basal soln., the Ge wave appears only when **I** is present. With a basal soln. of 0·2 *M* NaCl and 0·1 *M* pyridine or phenylarsonic acid, the Ge wave forms at a pH > 10. At pH 8, with a basal soln. of $Na_2B_4O_7$, **I**, or Na acetate, Na formate or oxalic acid together with **I**, the height of the Ge wave is proportional to the concn. of Ge ($0{\cdot}2 \times 10^{-4}$ to 4×10^{-3} *M*). It is recommended that the polarographic determination of Ge be carried out with a basal soln. of 0·2 *M* Na acetate at pH 7 to 9 ($E_{\frac{1}{2}} = -1{\cdot}42$ V). To remove O before polarography, add Na_2SO_3 and gelatin (0·002 to 0·005%) to the soln. The height of the wave is proportional to the Ge concn. ($< 4 \times 10^{-4}$ *M*). Separate Ge from interfering cations (except As) by extracting with CCl_4 from 9 *N* HCl. Re-extract and to the extract add 0·1 *N* iodine (3 drops) to oxidise As, and phenolphthalein (3 drops). Then add 0·1 *N* $Na_2B_4O_7$ (10 ml) or 0·5 *M* Na acetate (10 ml), dilute with H_2O to 50 ml, remove O, and record the polarogram from $-1{\cdot}0$ to $-1{\cdot}7$ V. K. R. C.

3684. **Complexometric titrations (chelatometry). LI. Direct determination of bivalent tin.** J. Dubský (Bižuterie, Jablonec nad Nisou, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 4045–4048 (in Russian).—The fact that bivalent tin can be masked with small amounts of NH_4F from reaction with EDTA (disodium salt) (**I**) as well as methylthymol blue, is the basis of a complexometric determination of Sn^{II} in the presence of Sb^{III} in a medium of NH_4F - tartaric acid. *Procedure*—To a soln. containing ≃ 50 mg of Sn^{II}, 50 mg of Sn^{IV} and 10 mg of Sb^{III} is added NH_4F (0·1 g) and (only if Sb is present) tartaric acid (about 0·02 g). The pH is brought to 5·5 to 6 with a pyridine acetate buffer soln. (40 ml of anhyd. acetic acid and 160 ml of pyridine diluted to 1 litre with H_2O), and the soln. is titrated with **I** till the blue colour of methylthymol blue changes to yellow. J. ZÝKA

3685. **Determination of iron in tin of 99·999 per cent. purity.** G. Bradshaw and J. Rands (Capper Pass & Son Ltd., North Ferriby, Yorks., England). *Analyst*, 1960, **85**, 76–78.—To the sample is added conc. HCl and then, with cooling, a mixture of conc. HBr and Br (5:3). The mixture is warmed, the vessel is covered and the contents are allowed to evaporate on a hot-plate. When the liquid is almost dry the vessel is uncovered and the fumes of tin bromide are allowed to escape. The residue is dissolved in dil. HCl, the soln. is concentrated to one-half of its original vol., then cooled and treated with NH_4SCN and $(NH_4)_2S_2O_8$ soln. After adjustment of the liquid to a known vol., the extinction is measured in a Spekker absorptiometer with Ilford No. 603 filters, corrected for a blank determination and referred to a calibration graph. A. O. JONES

3686. **Use of naphthalene derivatives in inorganic analysis. VIII. The effect of substituents in the naphthalene nucleus on the fluorimetric detection of tin.** J. R. A. Anderson, J. L. Garnett and L. C. Lock (Univ. of New South Wales, Sydney, Australia). *Anal. Chim. Acta*, 1960, **22** (1), 1–7 (in English).—Fourteen nitro and nitroso derivatives of naphthalene are examined as spot-test reagents for Sn. Most of the compounds yield green, blue or purple fluorescent spots with 0·01 to 0·1 mg of Sn^{2+} in 0·01 ml of soln. in the procedure previously described (*cf.* Anderson and Garnett, *Anal. Abstr.*, 1958, **5**, 2568). It is shown that the most important factors relating structure of reagent to intensity of fluorescence are (*i*) the position of the nitro or nitroso group in the naphthalene nucleus, (*ii*) whether the group is sterically hindered and (*iii*) the electropositive or electro-negative characters of other substituent groups. H. N. S.

3687. **Molar extinction coefficients of dithizone and lead dithizonate in carbon tetrachloride.** O. A. Weber and V. B. Vouk (Inst. for Med. Res., Yugoslav Acad. Sci. and Arts, Zagreb, Yugoslavia). *Analyst*, 1960, **85**, 40–45.—The extinctions of extremely pure soln. of dithizone (prep. described) were measured at the primary and secondary absorption maxima and the absorption minimum of dithizone (620, 450 and 515 mμ, respectively) and at the absorption maximum of lead dithizonate (520 mμ). The soln. of lead dithizonate was prepared by extracting a standard soln. of Pb with a soln. of dithizone in CCl_4. The extinction was then measured at the absorption max. of Pb dithizonate and at that of dithizone. The concn. of the dithizone soln. was determined by removing the solvent in an electrically heated apparatus (described) and weighing the residue. The concn. of the Pb dithizonate soln. was determined by evaporation, destruction of organic matter in the residue, and polarographic determination of Pb in the residue, with succinic acid as supporting electrolyte. The results are tabulated. A. O. JONES

3688. **Extraction constant of lead dithizonate.** V. B. Vouk and O. A. Weber (Inst. for Med. Res., Yugoslav Acad. Sci. and Arts, Zagreb, Yugoslavia). *Analyst*, 1960, **85**, 46–51.—The extraction of lead as its dithizone complex into CCl_4 was investigated in the pH range 5 to 11 by the use of three aq. buffer soln. containing aq. NH_3 and citrates or cyanides. Dithizone was dissolved in water-saturated CCl_4, the soln. was equilibrated with an aq. soln. of Pb, and the extinction of the organic layer was measured at 620 and 520 mμ. By substituting previously obtained values for the extinction coeff. and solving the equation for two light-absorbing components, the concn. of Pb dithizonate and free dithizone were calculated. The extraction constant of Pb dithizonate is $1{\cdot}4 \times 10^{-3}$ in the presence of citrates and $2{\cdot}9 \times 10^{-4}$ in the presence of cyanides. The reaction between dithizone in CCl_4 and Pb^{2+} is extremely rapid.
A. O. JONES

3689. **Complexometric determination of lead.** O. B. Budevskiĭ. *Zavod. Lab.*, 1960, **26** (1), 50–51.—The sample (0·2 to 0·25 g) of lead concentrate or ore is heated first with 10 to 15 ml of conc. HCl and then with 5 ml of conc. HNO_3 and the soln. is evaporated to fuming with 10 ml of dil. H_2SO_4 (1:1). Water (5 ml) is added and the evaporation is repeated. The residue is boiled with water (100 to 150 ml) and the soln. is kept cold for 2 hr. The ppt. of $PbSO_4$ is collected and washed with 1% H_2SO_4 soln. and then dissolved in 5 ml of a soln. prepared by adding 200 g of KOH in small portions to a soln. of 100 g of tartaric acid in 500 ml of water and diluting the cooled soln. to one litre. Dissolution is completed by transferring the filter to the beaker together with 10 ml of water and heating for 5 to 10 min. if $BaSO_4$ is absent and for 45 min. if $BaSO_4$ is present. The soln. is then diluted to 75 ml, mixed with the indicator (a 0·5% soln. of methylthymol blue in KNO_3 soln.) and treated dropwise with HCl until the colour changes to blue (pH 6·7). A ppt. of $Pb(OH)_2$ does not interfere. After addition of 1 g of hexamine the soln. is titrated with 0·025 *M* EDTA (disodium salt). G. S. SMITH

3690. **Polarographic determination of 10^{-7}*M* lead.** A. G. Stromberg and V. E. Gorodovykh (Tomsk Polytech. Inst.). *Zavod. Lab.*, 1960, **26** (1), 46–48.—Two types of stationary mercury electrodes were used with similar results. One, in the form of a hanging drop, is obtained by use of a platinum-wire cathode, 0·5 mm long, and electrolytic deposition of the Hg from saturated $Hg(NO_3)_2$ soln. with a current of 63 mA for 3 min. The other is a mercury drop contained in a small cup. To determine 10^{-5} to 10^{-7} *M* Pb, the soln. (100 ml) in 0·1 *N* KCl is freed from O and electrolysed for 20 min. at −0·8 V *vs.* the S.C.E. An anodic peak due to Pb is then recorded whilst the potential is brought to zero at a rate of 200 to 400 mV per min. The height of the peak is proportional to the concn. of Pb. The method can be used in the presence of a large excess of Zn. The effect of duration of electrolysis on the peak height was studied with 10^{-6} *M* $PbCl_2$. The drop had a surface area of 10 sq. mm. The peak height rose to a max. at 25 min. and then decreased.
G. S. SMITH

3691. **Determination of lead in lead-brass [Muntz metal].** I. E. Bykov and L. S. Gorshkova. *Trudy Inst. Metallurg. Ural'sk. Filial Akad. Nauk SSSR*, 1959, (3), 127–129; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4637.—The method is based on the pptn. of Pb (≃ 1%) as $PbCrO_4$ followed by polarography after reducing Cr^{VI} with ascorbic acid. *Procedure*—Dissolve 0·5 g of the sample in 5 ml of HNO_3 (1:1), evaporate the soln. till a film of salts appears, and re-dissolve by heating with a few ml of hot water, adding dil. HNO_3 (1:1) dropwise if necessary. Dilute the resulting soln. with hot water to ≃ 50 ml, heat to boiling-point, add 5 ml of hot 2% $K_2Cr_2O_7$ soln. and boil for several minutes to obtain a coarse-grained ppt. of $PbCrO_4$. Cool, filter off the ppt., wash it twice with water and dissolve it in 10 ml of dil. HCl (1:1). Add 25 mg of ascorbic acid, set aside until the soln. is colourless, add 2 ml of 0·25% gelatin soln., dilute to 50 ml and polarograph without removing O. The determination may also be carried out by titrating the excess of $Cr_2O_7^{2-}$ with $(NH_4)_2SO_4.FeSO_4.6H_2O$ or iodimetrically.
C. D. KOPKIN

3692. **Photometric determination of bismuth in refined lead.** R. A. Karanov and A. N. Karolev (Lead-Zinc Works, Kirjali, Bulgaria). *Zavod. Lab.*, 1960, **26** (1), 48–50.—The thiourea method of Lur'e and Ginzburg (*Zavod. Lab.*, 1949, **15**, 21) is modified to permit the determination of small amounts of Bi (0·001 to 0·10%) in the presence of large amounts of Pb (major element) and Sb. For dissolution of the sample of lead, 10 g is dissolved in 35 ml of HNO_3 (1:2) when the concn. of Bi is between 0·001 and 0·010%, 2 g is dissolved in 10 ml of HNO_3 (1:2) when the concn. is between 0·010 and 0·045%, and 1 g is dissolved in 10 ml of HNO_3 (1:5) when the concn. is between 0·045 and 0·090%. In the presence of > 5 mg of Sb, 1 to 2 g of tartaric acid is added. After removal of oxides of N, the soln. is diluted to 75 ml, then mixed with 20 ml of 10% thiourea soln. and diluted to 100 ml. If the concn. of Pb is between 2 and 10%, the soln. is heated to 27° to 28° and the extinction of the filtered soln. is measured at 25°. If the concn. of Pb is 10%, the soln. is heated to 32° to 33°, filtered, and examined at 29°. By this means the Pb complex which would otherwise adsorb Bi is retained in soln.
G. S. SMITH

3693. **Standard titanium - hydrogen samples.** M. J. Trzeciak (Battelle Mem. Inst., 505 King Ave., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 72–74.—Equipment and technique are described for the preparation of titanium samples having known hydrogen contents. (*Cf. U.S. Atomic Energy Comm.*, Rep. DMIC-Memo-9, 1959; *Anal. Abstr.*, 1959, **6**, 4339.)
T. R. ANDREW

3694. **Spectrophotometric determination of titanium with 2:3:7-trihydroxy-9-methyl-6-fluorone.** A. K. Majumdar and C. P. Savariar (Dept. Inorg. and Anal. Chem., Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, **21** (6), 584–587 (in English).—In acid soln. 2:3:7-trihydroxy-9-methyl-6-fluorone reacts with Ti^{IV} to give a rose-red colour (max. absorption at 520 mμ). The extinction is constant in the pH range 1·7 to 2·1, and for at least 24 hr.; 0·25 p.p.m. of Ti^{IV} gives an extinction of 0·3 in a 1-cm cell.
T. R. ANDREW

3695. **Spot tests for the identification of titanium alloys and their differentiation from zirconium and its alloys.** H. C. J. Saint (I.C.I. Ltd., Metals Div., Witton, Birmingham, England). *Anal. Chim. Acta*, 1960, **22** (1), 50–55 (in English).—A drop of solvent (fluoroboric acid or a mixture of hydrofluoric and nitric acids) is applied to the alloy, followed by a selective reagent for the alloying metal. Methods

are described for identifying Sn, Mn, V, Cu and Mo in titanium alloys, and for distinguishing zirconium alloys from titanium alloys. H. N. S.

3696. **Indirect titrimetric determination of zirconium and hafnium in their oxide mixture.** L. J. Ottendorfer (Inst. of Inorg. and Gen. Chem., Univ. of Technol., Vienna, Austria). *Chemist Analyst*, 1959, **48** (4), 97 and 105.—Fuse a mixture of ZrO_2 and HfO_2 (0·15 g), *e.g.*, that obtained by ignition of a mandelate or *p*-bromomandelate ppt., with $Na_2S_2O_7$ (1 g, a further 1 g being added during fusion). Allow the melt to cool and dissolve it, without heating, in 0·05 *M* EDTA (disodium salt) (25 ml) and *N* HCl (25 ml). Adjust the pH to between 2·5 and 3·5 with ammonium acetate and titrate the soln. with a standard soln. of Th [27·6 g of $Th(NO_3)_4.4H_2O$ in 1 litre of soln. at pH 2·5 to 3·5], to xylenol orange. Then, ZrO_2 (%) = 29·71 VM/w − 141·12, where V = vol. (ml) of EDTA used of molarity M, and w = wt. (g) of mixed oxides.
G. S. Roberts

3697. **Spectrophotometric determination of thorium with neothorone [arsenazo].** Takeo Takahashi and Shingo Miyake (Inst. of Ind. Sci., Univ. of Tokyo, Yayoi-cho, Chiba-shi, Japan). *Talanta*, 1959, **3** (2), 155–159 (in English).—Conditions for the determination of Th in aq. soln. with an aq. 0·1% soln. of arsenazo have been established. The sample soln. is buffered to pH 2, set aside for 1 hr. after the addition of the reagent, and the extinction is measured at 580 mμ at room temp. Beer's law is obeyed from 0 to 150 μg of Th per 25 ml; Zr, Ti, Ce, UO_2^{2+}, Fe, F, PO_4^{3-}, oxalate, NO_3^- and citrate interfere.
G. Burger

3698. **Rapid determination of thorium in ores. III. Determination of microgram amounts of thorium in ilmenite sands.** V. T. Athavale, K. P. Oke and M. M. Tillu (Anal. Div., Atomic Energy Estab., Trombay, Bombay, India). *Anal. Chim. Acta*, 1959, **21** (6), 528–531 (in English).—The sample (1 g) is fused with Na_2O_2 and the cooled melt is extracted with water and neutralised with HCl. If Ti or Zr is absent, $Zr(NO_3)_4$ (≃ 10 mg of ZrO_2) is added and Th and Zr are pptd. with aq. NH_3. The ppt. is filtered off and transferred to a platinum dish, together with the ash of the ignited filter-paper, and Si is removed by evaporation with HF. The soln. is diluted with 30 ml of water, and $La(NO_3)_3$ is added (≃ 10 mg of La_2O_3). The pptd. fluorides are set aside overnight, then filtered off. The ppt. and paper are charred, but not ignited, in a platinum dish, then carbon is burnt off at 600°. The residue is taken to dryness with H_2SO_4 (0·5 ml), and taken up, after successive evaporations to dryness with HNO_3, in 2 ml of HNO_3 (1:1) and 5 ml of water. After addition of 5 drops of H_2O_2, 0·5 ml of 10% oxalic acid soln. and $Hg(NO_3)_2$ (≃ 5 mg of HgO) as carrier, Th is pptd. as the iodate before spectrophotometric determination with thoron. The recovery of Th (8 to 60 μg) is within ±10% of the added amount.
T. R. Andrew

3699. **Determination of ammonia in the presence of nitrites.** G. P. Aleksandrov and V. S. Tikhonova (Inst. of Geology of Useful Minerals, Acad. Sci., UkrSSR). *Zavod. Lab.*, 1960, **26** (1), 57.—When NO_2^- are present the determination of NH_3 by distillation from an alkaline soln. must be preceded by the oxidation of NO_2^- to NO_3^-. For this purpose the soln. (100 to 150 ml) is made just acid to methyl orange with H_2SO_4 and then boiled for 10 to 15 min. with 3 to 5 ml of 30% H_2O_2. G. S. Smith

3700. **System for the analysis of nitrates and oxides of nitrogen.** F. Vrátný (Dept. Chem., Purdue Univ., W. Lafayette, Ind., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (6), 579–583 (in English).—Nickel at 800° reacts with oxides of N to give NiO and N. Mixed oxides of N, obtained for example by heating nitrates, are passed through a liquid-nitrogen trap to condense N_2O_3 and NO_2, and then through nickel-impregnated asbestos at 800°. The resulting N is measured, the NiO is reduced with H and the H_2O evolved is recorded; the ratio of N to O can then be calculated. After removal of the cold trap, similar techniques are applied to the mixture of N_2O_3 and NO_2.
T. R. Andrew

3701. **A critical study of the precipitation of ammonium phospho-12-molybdate.** P. Cannon (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Talanta*, 1960, **3** (3), 219–231 (in English).—Variables (concn. of HNO_3 and NH_4NO_3, temp., time of keeping the ppt. before removal from the soln., and method of drying) that influence the constancy of composition of the yellow ammonium molybdophosphate have been studied, and the optimum conditions for the quant. determination of PO_4^{3-} by this method have been established. The sample soln. should be ≃ 0·0015 *M* in PO_4^{3-}, with concn. of 0·08 *M* MoO_3, 0·1 *M* NH_4NO_3 and 1·5 *M* HNO_3. The stabilised molybdate reagent should be prepared as described. The pptn. should be made at 40° during 1 hr., and the mixture set aside for 24 hr. before filtration. It is preferable to add the phosphate soln. to the molybdate soln. because the hygroscopicity of the oven-dried ppt. is thereby reduced. Washing should be effected with 0·15 *M* NH_4NO_3 - 0·1 *M* HNO_3, followed by 0·1 *M* HNO_3 at 0°, and the ppt. should be dried at 130° for ≮ 2 hr. Provided that there is no deposition of MoO_3 from the reagents (checked with a phosphate soln. of known concn.), the ppt. can be weighed as $(NH_4)_3PO_4.12MoO_3$ with a coeff. of variation of < 0·3%. This recommended procedure takes rather more than one day to complete; if max. accuracy is required it should be used only as a preliminary separation before determining P as $Mg_2P_2O_7$.
W. J. Baker

3702. **A method of analysis of oxygen isotopes in orthophosphate—its use in the measurement of palaeotemperatures.** A. P. Tudge (Dept. of Chemistry, Univ. Chicago). *Geochim. et Cosmoch. Acta*, 1960, **18** (1–2), 81–93.—Details are given for the dissolution of phosphatic shells, the purification of the phosphate and its final precipitation as $BiPO_4$. The phosphate oxygen is released by reaction with BrF_3, purified, and analysed mass-spectrometrically for the determination of the ^{18}O to ^{16}O ratio. The method is quant., free from isotopic fractionation and exchange, and precise to ±0·15%. A correction can be made for the contaminating effect of water oxygen introduced during the hydrolysis of condensed phosphates.
R. A. Howie

3703. **Infra-red spectra of inorganic phosphorus compounds.** J. V. Pustinger, jun., W. T. Cave and M. L. Nielsen (Monsanto Chemical Co., Res. Dept., Dayton, Ohio, U.S.A.). *Spectrochim. Acta*, 1959, (11), 909–925.—The spectra of 55 compounds, including orthophosphates, phosphofluoridates, pyrophosphates, imidodiphosphates and metaphosphimates, are presented. The compounds were

examined in the anhydrous state in the form of liquid paraffin and hexachlorobutadiene mulls. The appearance of the N–H stretching band at 3100 cm^{-1} in cyclic phosphorus - nitrogen compounds suggests the structure to be (–P(O).NH–), rather than that previously postulated (–P(OH):N–) (*cf.* Corbridge and Lowe, *J. Chem. Soc.*, 1954, 493). E. G. CUMMINS

3704. **New method for the photometric determination of arsenic.** G. Ciuhandu and M. Rocsin (Toxicol. Lab., Inst. of Hygiene, Timişoara, Romania). *Z. anal. Chem.*, 1960, **172** (4), 268–274 (in German).—Alkaline soln. of the Ag complex of *p*-sulphamoylbenzoic acid are rapidly reduced by AsH_3 with the quant. formation of a coloured sol. The extinction of the sol at 420 mμ is proportional to the amount of As up to 100 μg. *Procedure*—To the 5-ml sample (1 to 150 μg of As) in a centrifuge tube add 50% H_2SO_4 (1 ml) and granulated zinc (0·5 to 0·6 g) and lead the evolved gas through 5 ml of a mixture of 0·1 *M* Na *p*-sulphamoylbenzoate, 0·1 *M* $AgNO_3$ and *M* NaOH (2:2:1). Pass the gas for 1 hr. at 20°, then determine the extinction of the sol at 420 mμ in a Pulfrich photometer.

J. P. STERN

3705. **Studies on the spectrochemical determination of arsenic.** I. Benkő and M. Kulcsár (Res. Inst. for Heavy Chem. Ind., Veszprém, Hungary). *Magyar Kém. Foly.*, 1959, **65** (12), 460–463.—The sample is absorbed in a carrier consisting of lead oxide and spectroscopically pure carbon (1:1); the evaporation of As is thus slowed down by the formation of lead arsenide. The carbon electrode used as anode has an external diameter of 5 mm and a crater 7 mm deep with a diameter of 4 mm. A d.c. arc with a 10-amp. current is used for excitation. For the accurate determination of As, Te can be added to the carrier; its ionisation potential is close to that of As and even in 1% concn. it has strong lines (2382·3 and 2385·8 A) near to that of As (2349·8 A). This method has been used for the determination of As_2O_3 in germanium dioxide; after a 100-fold chemical enrichment, even 0·1 p.p.m. of As_2O_3 can be determined and 0·03 p.p.m. can be detected. Other arsenic compounds have a similar intensity of emission when the carrier is used. A. G. PETO

3706. **Ultra-violet spectrophotometric determination of bismuth with perchloric acid.** Yuroku Yamamoto (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1959, **8** (8), 513–518.—Bismuth gives an absorption max. at 220 mμ in 1 to 9·5 *N* $HClO_4$; with decrease in acid concn., the absorption curve becomes flat, the location of the max. remaining unchanged. It would appear that the hydrated bismuth ion is converted into an hydroxo complex at pH 1 to 3. The extinction is proportional to the concn. of Bi in *N* $HClO_4$ for < 15 p.p.m. The presence of NO_3^-, Cl^-, Fe^{III}, Sn and Sb affects the extinction, and Al causes a considerable change in the shape of the spectrum.

K. SAITO

3707. **Determination of bismuth based on the reduction of molybdophosphoric acid. An absorptiometric method.** R. H. Campbell and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 54–57.—Molybdophosphoric acid in 0·2 *M* H_2SO_4 is reduced by ascorbic acid, in the presence of Bi, to molybdenum blue (wavelength max. 725 mμ). The several variables of this reaction have been studied and a method is proposed for the determination of 0·02 to 1·2 mg of Bi. The interference of 21 ions is reported.

T. R. ANDREW

3708. **Micro-heterometric determination of bismuth by titration with thiocarbanilide [*sym.*-diphenylthiourea]. A study of the reaction and the compounds.** M. Bobtelsky and B. Carmon (Dept. Inorg. and Anal. Chem., The Hebrew Univ., Jerusalem). *Anal. Chim. Acta*, 1959, **21** (6), 515–523 (in English).—The titration of Bi^{III} with either *sym.*-diphenylthiourea (**I**) or I^-, in the presence of the other, gives rise to insoluble BiI_2I_3, whereas titration of mixtures of **I** and I^- with Bi^{III} gives BiI_4I_4. Best results are obtained by titrating Bi^{III} (≃ 0·2 mg) in 20 ml of soln. containing 1 ml of *N* HNO_3, 1 ml of 0·5 *M* $Mg(NO_3)_2$, $Zn(NO_3)_2$ or $Al(NO_3)_3$, and 8 ml of 0·004 *M* **I** in 50% ethanol with 0·0025 *M* KI. Some experiments were carried out in which the soln. was made 0·1 to 1 *M* in 14 cations without adverse affect.

T. R. ANDREW

3709. **Electro-analysis by the use of EDTA. II, III. Determination of bismuth and lead.** Hisao Hayakawa (Fac. of Educ., Kobe Univ., Sumiyoshi, Higashinada-ku). *Japan Analyst*, 1959, **8** (7), 449–452.—Bismuth (50 to 100 mg) is quant. deposited on a platinum cathode within 2 hr. from an aq. soln. (≃ 200 ml) of pH 3·5 to 5·5 in the presence of EDTA (at a molar ratio to Bi of ≃ 2) and hydrazine dihydrochloride (1 g) at 60° (terminal voltage, 1·2 V). Lead (< 180 mg) is also deposited on a platinum cathode at 40° from a similar soln. of pH 6 to 7.

IV, V. Determination of silver and mercury. Hisao Hayakawa. *Ibid.*, 1959, **8** (8), 487–491.—Silver (< 150 mg) is deposited, free from Cu, on a platinum cathode at 50° from an NaOH soln. of pH 9 to 10·4 in the presence of EDTA (at a molar ratio to the sum of Cu and Ag of > 2) (1·2 to 2 V, 2 hr.). Mercury (60 to 120 mg) is deposited quant. on a silver-plated platinum electrode from a Na_2CO_3 - EDTA soln. of pH 3 to 5. Copper (< 150 mg) is masked with EDTA (at a molar ratio to the sum of Cu and Hg of > 2). K. SAITO

3710. **Determination of bismuth and bivalent heavy metals in the presence of each other.** L. Barcza and E. Körös (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Chemist Analyst*, 1959, **48** (4), 94–95.—The EDTA complexes of heavy metals, except those of Bi and Hg, are unstable at pH 1. Thus Bi may be determined in mixtures from which Hg is absent by titration at pH 1, the other metals being titrated after adjustment of the soln. to a pH of 5 to 6. The indicators xylenol orange and methylthymol blue are satisfactory at both pH levels. Several methods are suggested for the titration of Bi and Hg in mixtures. Mercury can be masked by SCN^- while the Bi titration is carried out, then the $[Hg(SCN)_4]^{2-}$ complex can be decomposed by Ag^+ and the Hg^{2+} titrated at pH 5 to 6. Alternatively, Hg^{2+} can be titrated with KSCN soln. and Bi with EDTA after reduction of the Fe^{III} indicator with ascorbic acid. G. S. ROBERTS

3711. **Analytical applications of the complexones. XX. Spectrophotometric and absorptiometric microdetermination of vanadium with 1:2-di-(2-aminoethoxy)ethane-NNN′N′-tetra-acetic acid.** F. Bermejo Martínez and M. Paz Castro (Lab. de Quím. Anal. de la Fac. de Ciencias, Santiago de Compostela).

Inf. Quim. Anal., 1960, **14** (1), 20–23.—Vanadium reacts with this compound and H_2O_2 in acid soln. (pH 1·5 to 2·4) to give an orange - yellow colour the intensity of which is a linear function of the vanadium concn. up to 120 μg per ml. The extinction of the soln. is measured at 426 mμ, either absorptiometrically or spectrophotometrically. There is no interference from SO_4^{2-}, NO_3^-, Cl^-, Br^-, NH_4^+, Na^+, K^+ or small amounts of PO_4^{3-} and WO_4^{2-}. G. H. FOXLEY

3712. **Determination of niobium in the parts per million range in rocks.** F. S. Grimaldi (U.S. Geological Survey, Washington 25, D.C.). *Anal. Chem.*, 1960, **32** (1), 119–121.—A modified thiocyanate method is described for Nb. Simple techniques are described for the separation of possible interferences. Results are tabulated for granite G-1 (containing 0·00217% of Nb, standard deviation 0·00009 for 10 determinations) and diabase W-1 (containing 0·00096% of Nb, standard deviation 0·00006 for 10 determinations). T. R. ANDREW

3713. **Separation of niobium and tantalum from zirconium with salicylhydroxamic acid.** A. K. Majumdar and A. K. Mukherjee (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (1), 25–26 (in English).—*Procedure*—To a soln. of ZrO_2 (9 to 180 mg) and Nb_2O_5 (10 to 240 mg), containing 5% (v/v) of H_2SO_4 and 5 to 10% of H_2O_2 (20 vol.), add an excess of a freshly prepared 1% soln. of salicylhydroxamic acid (**I**) in hot water. Add dil. aq. NH_3 until the pH is > 2·5, filter off the ppt., wash with a 0·1% soln. of **I** containing 1% of NH_4NO_3, ignite, and weigh as ZrO_2. For re-pptn., fuse the ZrO_2 with $KHSO_4$, extract with H_2SO_4 - H_2O_2 soln. and proceed as described above. Determine Nb in the filtrates by pptn. with cupferron or N-benzoyl-N-phenylhydroxylamine. The method is not satisfactory for the separation of Zr from Ta. H. N. S.

3714. **Separation of niobium from tantalum by extraction as tributylammoniumniobium thiocyanate.** M. Ziegler, O. Glemser and A. von Baeckmann (Inorg. Chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1960, **172** (2), 105–115 (in German).—Methods for the extraction of Nb and Ta are investigated. The sample is decomposed by fusion with $K_2S_2O_7$ in a platinum crucible. The fused mixture is transferred into a reaction flask (apparatus described), and thiocyanate and tributylammonium ions are added in a current of SO_2. Niobium is extracted with *iso*amyl acetate and determined photometrically by a method similar to that of Palilla *et al.* (*Anal. Chem.*, 1953, **25**, 926). B. B. BAUMINGER

3715. **Electrometric determination of dissolved oxygen in aqueous solution.** G. S. James and M. J. Stephen (Dept. of Chem. and Chem. Engng, Univ. of Witwatersrand, Johannesburg, South Africa). *Analyst*, 1960, **85**, 35–39.—The method depends on the reactivity of chromous ions towards oxygen. The chromous reagent is electrolytically prepared in the sample soln. and, by the use of the apparatus described, the excess of chromous ions, and hence the end-point of the coulometric titration, can be detected. Results are accurate to within 2% at concn. as low as 0·03 p.p.m. of oxygen. The method has the advantage that no standard soln. and only one de-oxygenated soln. are required. A. O. JONES

3716. **Determination of oxygen in metals and oxides by means of sulphur chloride. III. Determination of oxygen in chromium, titanium and zirconium oxides and in certain metals and alloys.** K. E. Kleiner and N. V. Obolonchik. *Ukr. Khim. Zhur.*, 1959, **25** (3), 370–373; *Ref. Zhur., Khim.*, 1960, (1), Abstr. No. 866.—The possibility is shown of determining O in ZrO_2, TiO_2, Cr_2O_3, copper, cadmium, nickel, chromium, titanium, zirconium, and nickel - molybdenum and nickel - tungsten alloys by a previously described method (*cf.* Kleiner, *Anal. Abstr.*, 1958, **5**, 471) from the amount of SO_2 formed on ignition of the oxides or metals to between 600° and 900° in a current of N saturated with S_2Cl_2 vapour. It is shown that TiO_2 and Cr_2O_3 are quant. decomposed by S_2Cl_2 at < 600° and < 850°, respectively, with the formation of an equivalent amount of SO_2. Quartz boats (at 500°) or graphite boats (at higher temp.) may be used to determine O in ZrO_2, more reliable results being obtained with the latter. Each determination takes from 30 min. to 1·5 hr. To obtain small "analytical concentrates" (non-distilling residues) for the determination of O, the excess of the free metal (particularly Ti and Zr) is distilled as the bromide at between 600° and 800° in a current of N. The slight positive errors observed in the determination of O after bromination are ascribed to insufficient purification of the Br. It is suggested that in some cases Cl or iodine may be used for the distillation of the metals as halides. C. D. KOPKIN

3717. **Thermolysis of sulphides precipitated by sodium sulphide. I. Sulphides of arsenic, mercury, rhenium, antimony and molybdenum.** I. K. Taimni and S. N. Tandon (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1960, **22** (1), 34–37 (in English).—Thermolysis curves are determined for As_2S_3, HgS, Re_2S_7, Sb_2S_3, Sb_2S_5 and $MoS_3.2H_2O$, the sulphides having been prepared by pptn. with Na_2S soln. as in previous work (*cf.* Salaria, *Anal. Abstr.*, 1958, **5**, 2174). H. N. S.

3718. **Determination of sulphite and thiosulphate in presence of each other.** L. Szekeres and E. Sugár (Peterdy u. 12, Budapest VII, Hungary). *Z. anal. Chem.*, 1960, **172** (1), 35–38.—To an excess of 0·1 *N* KIO_3 - KI soln. (20 to 40 ml) is added an aliquot of the test soln. followed by 15 to 20 ml of 2 *N* HCl and the liberated iodine is titrated with 0·1 *N* $Na_2S_2O_3$. To a specified NaOBr soln. (prep. described) is added a second aliquot of test soln., and after 1 to 2 min. the soln. is acidified with HCl, KI is added and the iodine liberated by the excess of Br is titrated with 0·1 *N* $Na_2S_2O_3$. The calculation follows from the fact that 1 mole of sulphite requires 2 equiv. of iodine and 1 equiv. of Br, and 1 mole of thiosulphate requires 2 equiv. of iodine and 8 equiv. of Br. B. B. BAUMINGER

3719. **Oxidations with potassium permanganate in the presence of fluoride. II. Determination of quadrivalent selenium.** I. M. Issa and M. Hamdy (Chem. Dept., Cairo Univ., Egypt). *Z. anal. Chem.*, 1960, **172** (3), 162–167 (in English).—The soln. of selenite, containing 10 to 30 mg of Se, is mixed with an excess of 0·1 *N* $KMnO_4$ in the presence of 25 to 75 ml of 2% NaF soln. and 4 to 7 ml of 9 *N* H_2SO_4. After allowing the soln. to stand for 10 to 30 min. the excess of 0·1 *N* $KMnO_4$ is determined by titration with 0·1 *N* $Hg_2(NO_3)_2$. Alternatively, an excess of $Hg_2(NO_3)_2$ soln. may be added, followed by back-titration with 0·1 *N* $KMnO_4$. It is claimed that the error is ≯ ±1%. H. M.

3720. **Rapid determination of a small amount of selenium in sulphide ores.** Tadao Kitazato and Yuji Saeki (Metallurgy Dept., Mitsubishi Metal Mining Co., Otemach, Chiyoda-ku, Tokyo). *Japan Analyst*, 1959, **8** (7), 422–428.—The colorimetric determination of Se with 3:3′-diaminobenzidine (**I**) (*cf.* Cheng, *Anal. Abstr.*, 1957, **4**, 1189) was applied to the analysis of sulphide ores. Interference resulting from metal ions present in common ores is satisfactorily eliminated by the addition of EDTA. The colour is stable in toluene for 30 min., and the standard deviation is 0·0003 for 0·2% of Se; the time taken for an estimation is 3·5 hr. *Procedure*—Dissolve the sample (0·5 to 1 g) in HNO_3 (sp. gr. 1·40) (30 ml), filter and make up to 100 ml. Evaporate an aliquot (containing 5 to 20 μg of Se) to dryness, dissolve the residue in 0·1 *M* EDTA (15 ml), dilute to 40 ml, add aq. NH_3 soln. and dil. formic acid and adjust the pH to 2·5. Add **I** soln. (0·5%) (2 ml), set aside for 40 min., adjust the pH to 6, dilute to 50 ml and extract with toluene (10 ml); make photometric measurements at 420 mμ.
K. SAITO

3721. **Separation of tellurium(IV) and iron(III) by extraction with tributyl phosphate.** Seiichiro Hikime, Hitoshi Yoshida and Yasumitsu Uzumasa (Chem. Dept., Fac. of Sci., Hokkaido Univ., Sapporo). *Japan Analyst*, 1959, **8** (8), 531–535.—Although Fe^{III} is quant. extracted with tributyl phosphate (**I**) at pH 0·4 to 1·0 in the presence of a large excess of SCN^-, Te^{IV} is only partly extracted (5 to 20%) under the given conditions. The Te is back-extracted with 0·1 *N* HCl from the **I** layer, Fe remaining in the org. phase. Satisfactory separation of Te (< 1 mg) from > 100 times its wt. of Fe is thus effected.
K. SAITO

3722. **Oxidation with potassium permanganate in the presence of fluoride. I. Direct titration of quadrivalent tellurium with potassium permanganate in acid medium in the presence of sodium fluoride.** I. M. Issa and M. Hamdy (Fac. of Sci., Cairo Univ., Egypt). *Z. anal. Chem.*, 1960, **172** (2), 94–98 (in English).—In order to obtain a rough idea of the concn. of tellurite, a preliminary titration with 0·1091 *N* $KMnO_4$ is made in the presence of 10 ml of 0·2% NaF soln. and 5 ml of 9 *N* H_2SO_4. Another volume of tellurite soln. is mixed in a conical flask with not less than two equivalents of 0·0740 *N* $HgNO_3$, 50 to 75 ml of 2% NaF soln., 5 to 10 ml of 9 *N* H_2SO_4 and an amount of 0·25 *M* $CuSO_4$ such that the ratio of the latter to the Mn^{3+} formed at the end-point is 1:12. The mixture is then titrated with $KMnO_4$ soln. The effects of acidity, temp., NaF, and Te^{4+} to Hg_2^{2+} ratio are discussed and the results are given.
B. B. BAUMINGER

3723. **Adsorption of uranium from organic solutions by ion-exchange resins.** G. Jangg and A. Burker (Inst. f. chem. Technol. anorg. Stoffe, Tech. Hochsch., Wien). *Öst. ChemZtg*, 1960, **61** (1), 7–10.—Adsorption of U and NO_3^- from soln. in tributyl phosphate (**I**) - hexane increased with increasing H_2O content of the resin and decreased with increasing concn. of **I**. Adsorption was greatest on resin in the sulphate form, but no adsorption occurred from a soln. of U in octyl pyrophosphate - hexane on any of the resins tested. Results for $Zn(NO_3)_2$ in **I** - hexane gave good agreement between the observed adsorption of Zn and that calculated from the H_2O content of the resin and the partition coeff. of Zn between H_2O and the organic phase. This showed that no adsorption of neutral salt had taken place.
P. D. PARR-RICHARD

3724. **Volumetric determination of uranium after reduction by lead in dilute perchloric acid solution.** T. W. Steele (Gov. Metallurg. Lab., Univ. of the Witwatersrand, Johannesburg, S. Africa). *Analyst*, 1960, **85**, 55–62.—The sample, after being heated to 950° to expel sulphate, is fumed with $HClO_4$ and the diluted residue is boiled to expel Cl and cooled to < 8°. The liquid is treated with aq. cupferron soln. and is extracted with ice-cold $CHCl_3$, the extracts being discarded. The aq. layer is evaporated to fuming with HNO_3, which is then removed by repeated dilution and evaporation to fuming with the $HClO_4$ present. The diluted soln. is boiled to expel Cl, granulated lead is added and the mixture is boiled at constant vol. and cooled under conditions that provide an atmosphere of CO_2 above the surface of the liquid. The liquid is drained from the lead, which is washed with dil. $HClO_4$, ferric perchlorate (prep. described) is added and, after 15 min., dil. H_3PO_4. After further dilution the liquid is titrated with 0·05 *N* $K_2Cr_2O_7$, with Na diphenylaminesulphonate as indicator. Results agree with those of a gravimetric method to within −0·02 to +0·28%.
A. O. JONES

3725. **Determination of uranium by cathode-ray polarography.** E. Booth and E. A. Terry (U.K.A.E.A., Royal Arsenal, Woolwich, England). *Anal. Chim. Acta*, 1960, **22** (1), 82–87 (in English).—Cathode-ray polarography is applied to the determination of U in the concn. range 2×10^{-4} to 4×10^{-3} *M*. When *M* $HClO_4$ - 0·01 *M* HCl is used as the supporting electrolyte the results compare favourably with those obtained by conventional polarography. Molybdenum is the only element that interferes seriously when present in concn. similar to that of the U.
H. N. S.

3726. **Uranium analysis by gamma absorptiometry.** R. E. Connally (Hanford Atomic Products Operation, General Electric Co., Richland, Washington). *Nucleonics*, 1959, **17** (12), 98–102.—A soln. containing U is placed between a 30-mC source of ^{241}Am and a scintillation detector incorporating a NaI(Tl) crystal (2 cm in diameter by 0·5 mm in thickness). The output is connected to a 10-mV recorder from which the result may be obtained after 1 min. The presence of 200 μC per litre of ^{137}Cs - ^{137}Ba produces an error of −1% at a uranium concn. of 5 g per litre; up to 200 mC per litre may be tolerated if an additional measurement is made in the absence of the source of ^{241}Am. The effect of light elements is considered: a concn. of Al of 30 g per litre is equivalent to a concn. of U of 1 g per litre. The coeff. of variation in 30 tests for concn. of U from 25 to 100 g per litre was 0·15%.
G. J. HUNTER

3727. **Separation of uranium from iron and vanadium.** K. Singh and D. Patnaik (Ravenshaw Coll., Cuttack, India). *Proc. Indian Acad. Sci., A*, 1959, **50** (6), 358–362.—Uranium is separated from Fe and V, as a fluoride complex, by the photolytic use of sunlight. *Procedure*—The HNO_3 soln. containing ≃ 0·5 g of U_3O_8 and ≃ 0·125 g of Fe_2O_3 or ≃ 0·45 g of V_2O_5 is adjusted to pH 2·0 to 2·5 after the addition of 2·5 g of NH_4HF_2. Sufficient ethanol and water are added to give a vol. of 150 ml containing 30% of ethanol. The soln. are exposed to sunlight for 4 to 5 hr., when U is pptd. as $NH_4F.UF_4.H_2O$. The soln. are filtered and the residues

are washed with 10% aq. ethanol. The recovery of U (of at least 99·9% purity) is $\simeq$ 93·5%. (*Cf. Anal. Abstr.*, 1960, **7**, 3728.) J. H. WATON

3728. **Photolytic separation of uranium from aluminium and [from a mixture of] thorium, cerium and lanthanum.** K. Singh, Balaram Sahoo and D. Patnaik (Ravenshaw Coll., Cuttack, India). *Proc. Indian Acad. Sci., A*, 1959, **50** (2), 129–131.—When NH_4HF_2 is added to an aq. soln. of the nitrates of U and Al, a considerable proportion of the latter, if present in large excess, is pptd. as fluoride. The filtrate with 10% of ethanol is exposed to light and the U is pptd. as $NH_4F.UF_4.H_2O$ in which form 99% of the U of 100% purity is obtained. The same process has been applied to the separation of U from Th, Ce and La. By a single exposure for 4 hr., 93 to 95% of the U is recovered. N. E.

3729. **Direct determination of uranyl nitrate in tributyl phosphate.** V. Šraier (Dept. Nucl. Res., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 304–305 (in Russian).—*Procedure*—Mix the soln. of uranyl nitrate in tributyl phosphate [about 0·4 to 0·8 g of $UO_2(NO_3)_2$] with three times its vol. of ethanol and dilute to 50 ml. Add aq. NH_3 ($\simeq$ 5 *N*) slowly till a ppt. appears and then 5 ml in excess. Filter off the ppt., wash with ethanol, ignite the filter with the ppt. at 900° and weigh the U_3O_8. For 0·4 to 0·8 g of $UO_2(NO_3)_2$ the error is $\pm$0·38%, which increases for smaller amounts of $UO_2(NO_3)_2$. For the analysis of aq. $UO_2(NO_3)_2$ soln. in the presence of Al, the following procedure is recommended. Extract the aq. soln. of the sample [containing $\simeq$ 0·3 to 0·5 g of $UO_2(NO_3)_2$] three times with a 62% soln. of tributyl phosphate in CCl_4 and then with pure hexane. Wash the organic phase with a 40% soln. of NH_4NO_3. Extract the washings with a 10% soln. of tributyl phosphate in hexane, extract $UO_2(NO_3)_2$ from the organic phase with a hot saturated soln. of $(NH_4)_2SO_4$, extract tributyl phosphate from the aqueous phase with hexane and precipitate the uranium with aq. NH_3. J. ZÝKA

3730. **Determination of traces of impurities in uranium metal. III. Photometric determination of traces of nickel.** Masami Suzuki (Inst. Tech.-anal. Chem., Fac. of Engng, Nagoya Univ., Chikusa-ku). *Japan Analyst*, 1959, **8** (7), 432–435.—The extraction of the dimethylglyoxime complex of Ni with $CHCl_3$ (Nielsch, *Z. anal. Chem.*, 1953, **140**, 267; 1954, **143**, 272; *Anal. Abstr.*, 1956, **3**, 3058, 3060) was examined for use in the photometric determination (at 375 mμ) of Ni (5 to 50 μg) in uranium. The extraction is quant. from a citrate buffer of pH 7·6 to 8·2 and the extinction of the $CHCl_3$ layer is proportional to the concn. of Ni for $<$ 50 μg per 10 ml. The amount of dimethylglyoxime present does not affect the results, but an increase in the amount of ethanol (used as solvent for the dimethylglyoxime) increases the vol. of $CHCl_3$ required for extraction. Copper gives variable interference, but the small amount of Cu normally present in uranium has no adverse affect. *Procedure*—Dissolve the sample (4 g) in HNO_3 (3 ml), expel the excess of acid, add citric acid soln. (25%) (10 ml), adjust the pH to 8 with aq. NH_3 soln., dilute to 50 ml, add ethanolic dimethylglyoxime soln. (1%) (1 ml) and extract with $CHCl_3$. K. SAITO

3731. **Determination of free acid in uranium(VI) solutions by means of cation exchangers.** Z. I. Dizdar and I. D. Obrenović (Inst. Nucl. Sci. "Boris Kidrich", Belgrade, Yugoslavia). *Anal. Chim. Acta*, 1959, **21** (6), 560–563 (in English).—The soln. is passed through a cation-exchange resin (H^+ form) and the total acidity of the eluate is determined by titration. The U^{VI} is determined on a separate sample, and the amount of acid equiv. to the U^{VI} is deducted from the total acid to give the free acid. T. R. ANDREW

3732. **Determination of gases in plutonium, uranium and zirconium by vacuum fusion.** R. E. Taylor (Hanford Atomic Products Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (6), 549–555 (in English).—The gases evolved by dropping the sample into an iron or platinum bath, containing carbon, at 1900° under vacuum are collected for mass-spectrometric analysis. Results are quoted for H, N and O in the p.p.m. region on an unspecified weight of sample. T. R. ANDREW

3733. **Reactions of plutonium ions with ethylenediaminetetra-acetic acid.** O. L. Kabanova, M. A. Danuschenkova and P. N. Paleĭ (Vernadsky Inst. of Geochem. and Anal. Chem., Moscow, USSR). *Anal. Chim. Acta*, 1960, **22** (1), 66–75 (in French).—Spectrophotometric measurements indicate that, at pH 3 to 5, one mol. of EDTA (disodium salt) (**I**) reduces six PuO_2^{2+} to PuO_2^+. Conductimetric titration of PuO_2^+ with **I** demonstrates the formation of a 1:1 complex. With an excess of **I**, Pu^V is reduced slowly to Pu^{IV}, which also forms a complex with **I**. The probable course of these reactions is discussed. H. N. S.

3734. **Determination of the valence states of neptunium ions in solution by controlled-potential coulometry.** R. W. Stromatt (Hanford Lab. Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 134–135.—Quadrivalent Np is not oxidised nor is Np^V reduced at a platinum electrode in significant quantities. This fact has been used as the basis of methods for determining the stable oxidation states of Np in a single soln. and for determining total Np. The method described may be useful for systems containing other ions which are titrated at the applied potentials. K. A. PROCTOR

3735. **Quantitative analysis of mixtures of corrosive halogen gases by gas - liquid chromatography.** J. F. Ellis, C. W. Forrest and P. L. Allen (U.K.A.E.A., Capenhurst, Chester, England). *Anal. Chim. Acta*, 1960, **22** (1), 27–33 (in English).—A gas chromatograph for the analysis of corrosive halogen compounds is described and a diagram is provided. The pipework is of nickel. Kel-F polymer oil $[(C_2ClF_3)_n]$ is used as the liquid phase, supported on 30 to 60-mesh Fluon or on polytrifluorochloroethylene. Columns 4·5 ft. and 11·5 ft. long are used, with argon as the carrier gas, and the efficiency is 20 to 30 theoretical plates per foot; nitrogen is a suitable carrier for compounds other than HF. The detector is a Martin's gas-density balance with nickel-lined passages. Retention times are determined for ClF, HF, Cl, ClF_3, UF_6, Br, BrF_5, perfluoromethyl*cyclo*hexane and chloroundecafluoro*cyclo*hexane, and representative analyses are given for mixtures of ClF, Cl, ClF_3 and UF_6, and of ClF, HF, ClF_3 and UF_6. H. N. S.

3736. **Determination of water in "anhydrous" hydrofluoric acid.** K. Otto, M. Uhlíř and J. Peša (Res. Inst. Macromol. Chem., Brno, Czechoslovakia).

Chem. Prûmysl, 1959, **9** (11), 587–588.—The sampling of HF, without access of moisture, can be carried out by the use of a simple apparatus which consists of a transparent titration flask, a volumetric flask (both constructed from polyethylene) and a connecting needle-like tube. After the prior rinsing of the apparatus with HF, the sample is absorbed in a mixture of pyridine and methanol and titrated with Karl Fischer reagent. The use of a transparent vessel enables the end-point to be observed visually. The method is suitable for determining H_2O in samples containing $> 99{\cdot}5\%$ of HF. J. ZÝKA

3737. **Apparatus for pyrohydrolytic determination of fluorides.** J. G. Surak, D. J. Fisher, C. L. Burros and L. C. Bate (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn.). *Anal. Chem.*, 1960, **32** (1), 117–119.—The platinum apparatus used by Warf *et al.* (*Ibid.*, 1954, **26**, 342) has been replaced by a simple and inexpensive version made of nickel. Working diagrams are given. T. R. ANDREW

3738. **Rapid analysis of iron-pickling liquor. VI. Determination of sodium chloride in sulphuric acid pickling liquor.** Kimio Mukaewaki (Nippon Tokushu Steel Tube Co., Funato, Itabashi-ku, Tokyo). *Japan Analyst*, 1959, **8** (7), 453–454.—Caldwell and Moyer's method (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 38) was applied to the analysis of pickling liquor. Amyl acetate is as suitable as nitrobenzene for facilitating the coagulation of AgCl. There is no interference from < 1 g of $FeSO_4$, $< 0{\cdot}05$ g of Cr or $< 20\%$ (v/v) of H_2SO_4. *Procedure*—To the sample (5 ml) add HNO_3 (sp. gr. 1·42) (10 ml), $4{\cdot}8\%$ $AgNO_3$ soln. (5 ml) and amyl acetate (3 ml) and shake for 1 min.; add 10% $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. (3 ml) and titrate with $0{\cdot}25\%$ NH_4SCN soln. K. SAITO

3739. **Determination of periodate, iodate, bromate and chlorate ions in the presence of each other.** L. Szekeres (Chem. Inst., Veterinary High School, Budapest, Hungary). *Z. anal. Chem.*, 1960, **172** (4), 256–259.—The procedure previously described (*Anal. Abstr.*, 1959, **6**, 3502) is adapted, IO_4^- and BrO_3^- being selectively reduced in the presence of IO_3^- and ClO_3^-. The accuracy is within $\pm 1\%$ on $0{\cdot}1\ N$ solutions. *Procedure*—Take four 25-ml aliquots. To the first add conc. HCl (30 ml) and KBr (2 g), set aside for 30 to 60 min., add H_2O (100 ml) and then KI (1 g) and titrate with $0{\cdot}1\ N$ $Na_2S_2O_3$ to obtain the sum of the four anions. To the second add 2% KI soln. (30 ml), KBr (1 g) and $2\ N$ H_2SO_4 (50 ml), and titrate after 3 to 5 min. to obtain the sum of IO_4^-, IO_3^- and BrO_3^-. To the third add $NaHCO_3$ (1 g) and 3% H_2O_2 soln. (10 ml) and warm until gas evolution ceases; cool the soln., add 4% KI soln. (15 ml) and $2\ N$ H_2SO_4 (40 ml) and titrate after 3 to 5 min. to obtain the sum of IO_3^- and BrO_3^-. To the fourth add conc. HCl (5 ml) and KBr (1 g) and dilute after 10 min. with H_2O (25 ml); neutralise with $5\ N$ NaOH (10 ml), add $NaHCO_3$ (3 g) and 2% aq. urea soln. (20 ml), and warm on the water bath for 15 min. Cool, add 2% KI soln. (30 ml) and $10\ N$ H_2SO_4 (10 ml), and titrate to obtain the IO_3^- content. J. P. STERN

3740. **Volumetric determination of manganese in cast iron and steel by the method of Lingane and Karplus.** J. F. W. Tertoolen, C. Buijze and G. J. van Kolmeschate (Anal. Inst. T.N.O., Postbus 49, Delft, Holland). *Chim. Anal.*, 1960, **42** (1), 9–14.—The method of Lingane and Karplus (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 8) for the dead-stop titration of Mn^{II} to Mn^{III} in pyrophosphate soln. with silver electrodes, is used. The interference of graphite and its oxidation products produced by dissolving the sample in HNO_3 is eliminated by filtration before dilution or the addition of reagents. The interference of V is eliminated with NaF, though W can interfere. All irons and steels can be analysed by this method except those containing $V > 4\%$; $V > 2\%$ in the presence of 2% of W (or vice versa), with Co absent; $V > 0{\cdot}5\%$ in the presence of $0{\cdot}5\%$ of Co (or vice versa); $Co > 0{\cdot}5\%$. *Procedure*—(*i*) With V and Co present the metal is dissolved in 50 ml of aqua regia and the soln. is boiled with 5 g of NaF. (*ii*) With $V < 4\%$ (W and Co absent) or $V < 2\%$ and $W < 2\%$ (Co absent), 7 g of NaF is added to the soln. which is then boiled for 15 min. (*iii*) With $< 0{\cdot}5\%$ of V, 5 g of NaF is added and the soln. is boiled for 2 min. In all cases 0·5 g of sulphamic acid is added to the cooled soln. to destroy HNO_2, and the soln. is filtered through cotton wool. After dilution to 150 ml, 14 g of Na citrate and 18 g of $Na_4P_2O_7$ are added. The ppt. is dissolved by adding aq. NH_3 and the pH is adjusted to 4 to 5. The soln. is then titrated with $0{\cdot}1\ N$ $KMnO_4$ to a dead-stop end-point. A circuit diagram for the titrimeter is given. E. J. H. BIRCH

3741. **Coulometric titration with higher oxidation states of manganese. Electrolytic generation and stability of tervalent manganese in sulphuric acid media.** R. G. Selim and J. J. Lingane (Dept. of Chem., Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (6), 536–544 (in English).—Spectrophotometric examination of soln. in H_2SO_4 indicates that the equilibrium constant for the reaction $2Mn^{III} \rightarrow Mn^{II} + Mn^{IV}$ varies from 10^{-3} in $4\ M$ H_2SO_4 to 10^{-4} in $7{\cdot}2\ M$ H_2SO_4. The efficiency of electrolytic generation of Mn^{III} in $5\ M$ H_2SO_4 is a function of current density and concn. of Mn^{II}, rising to $> 99\%$ for $> 0{\cdot}1\ M$ Mn^{II} at a current density between 1 and 3 mA per sq. cm. Results for other concn. of H_2SO_4 are similar. T. R. ANDREW

3742. **Oxidation with manganate solutions. I. Reduction of manganate with tervalent arsenic.** I. M. Issa, H. Khalifa and M. G. E. Allam (Fac. Sci., Cairo Univ., Egypt). *Z. anal. Chem.*, 1960, **172** (1), 21–28 (in English).—Manganate soln. prepared by the reduction of MnO_4^- with formic acid in N NaOH are fairly stable in $0{\cdot}015\ M$ concn. in presence of N NaOH. Titration of arsenite with manganate in the presence of telluric acid and $0{\cdot}1$ to $0{\cdot}2\ N$ NaOH yields results deviating by $\simeq -0{\cdot}77\%$ from the theoretical values. In the absence of telluric acid no satisfactory results were obtained.

II. Reduction of manganate with quadrivalent tellurium. I. M. Issa, M. G. E. Allam and M. M. A. Amer. *Ibid.*, 1960, **172** (2), 87–94.—The method consists in mixing the tellurite with an excess of manganate soln. in the presence or absence of telluric acid and $0{\cdot}25$ to $2\ N$ NaOH. The mixture is set aside for a few minutes, then an excess of oxalic acid is added together with an amount of H_2SO_4 sufficient to neutralise the alkali and bring the acidity to N. After heating to 60°, the excess of oxalic acid is titrated with $KMnO_4$ soln. Representative results are shown; the error is $\gtrsim \pm 0{\cdot}75\%$. B. B. BAUMINGER

3743. **Successive determination of iron and aluminium in chromium refractory and ore with 8-hydroxyquinoline, EDTA and CyDTA [1:2-diaminocyclohexane-NNN'N'-tetra-acetic acid].** Yoshihide Endo and Hajime Takagi (Fukiai Plant, Kawasaki Steel Co-op., Wakihama, Fukiai-ku, Kobe). *Japan Analyst*, 1959, **8** (8), 491–495.—Both Fe^{III} and Al are pptd. with 8-hydroxyquinoline (**I**) from an ammoniacal soln. in the presence of EDTA, which masks Cr. The ppt. is dissolved in dil. HCl and the Fe is titrated with standard EDTA soln., at pH 2·0 to 2·2, with **I** as indicator (dark green to yellow). Successive titration of Al with 1:2-diaminocyclohexane-NNN'N'-tetra-acetic acid (**II**) at the same pH, with Cu^{2+} - 1-(2-pyridylazo)-2-naphthol as indicator, is not affected by **I**. There is no interference from Ti (< 2·5 mg), Ca or Mg. *Procedure* —Fuse the sample (0·2 g) with $KHSO_4$, dissolve the melt in dil. HCl, oxidise the Fe with HNO_3, add 0·1 *N* EDTA (2 to 3 ml in excess of the vol. equivalent to the sum of Fe, Al, Mn, Ca, Mg and Cr) and ammonium acetate (**III**) soln. (25%) (10 ml), adjust the pH to between 4 and 6 and boil the soln. for 2 min. Add a 20% excess of **I** soln. (5% in dil. acetic acid), make the soln. ammoniacal and filter after 10 min. Wash the ppt. with an ammoniacal soln. containing **III**, dissolve it in HCl (1:1), dilute the soln. to 200 ml, add **III** soln. (10%) (10 ml), adjust the pH to between 2·0 and 2·2, and titrate the Fe with 0·05 *N* EDTA. Add 0·05 *M* Cu^{2+} (1 ml) and 1-(2-pyridylazo)-2-naphthol soln. (0·1%) (3 drops) to the product, and titrate the Al with 0·05 *N* **II**. K. SAITO

3744. **Quantitative analysis of Fischer - Tropsch catalysts by X-ray diffraction. Determination of alpha-iron, magnetite and iron carbides.** F. H. Herbstein, J. Smuts and J. N. Van Niekerk (Nat. Phys. Res. Lab., Pretoria, S. Africa). *Anal. Chem.*, 1960, **32** (1), 20–24.—The sensitivity and accuracy of X-ray diffraction methods in catalyst analysis have been studied. When a diffractometer is used the estimated coeff. of variation are 3 to 10%, and the limits of detection vary from 1 to 5% (w/w). Pure samples of the reference materials are not essential. The analysis time varies from 4 to 6 hr. depending on whether or not the elementary composition of the sample is known. K. A. PROCTOR

3745. **Resorcinol as a reagent for the spectrophotometric determination of ferric iron.** G. S. Rao (Dept. Chem., Univ. Saugar, India). *Anal. Chim. Acta*, 1959, **21** (6), 564–568 (in English).—Resorcinol reacts with Fe^{III} to give a soln. that is stable for 5 hr. at room temp. and has max. absorption at 550 mμ. The colour reaches a max. intensity at pH 3·2 [pH 2·9 given in text]. Chloride, Br^-, I^-, NO_3^- and SO_4^{2-} may be tolerated at 5000 p.p.m.; 38 interfering ions are reported. T. R. ANDREW

3746. **Analytical applications of xylenol orange. IV. Spectrometric study of the ferric - xylenol orange complex.** K. L. Cheng (Kelsey-Hayes Co., New Hartford, N.Y., U.S.A.). *Talanta*, 1959, **3** (2), 147–150 (in English).—Xylenol orange forms with Fe^{3+} in 0·05 *N* $HClO_4$ a purple - red 1:1 complex with an absorption max. at 550 mμ, which is suitable for the determination of Fe^{3+} in amounts between 5 and 50 μg. Interference is caused by F^-, Cl^-, citrate, PO_4^{3-}, SO_4^{2-}, H_2O_2, Bi, Mo, Zr, Nb and Sn. Some of the interfering metals can be masked. G. BURGER

3747. **Spectrographic analysis of high-alloy and complex steel. I. Procedure.** E. L. Grinzaid and F. D. Korobko. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 84–90; *Ref. Zhur., Khim.*, 1960, (1), Abstr. No. 876.—A procedure is evolved for the analysis of complex steel; particular attention is given to the choice of pairs of analytical lines free from superimposition. The spectra are excited in a high-voltage condensed spark from generator IG-2 with a carbon counter-electrode sharpened to a truncated cone. In analyses requiring localisation of the discharge (*e.g.*, for seam welds) a high-voltage spark-discharge from generator DG-1 with a copper electrode is used. The spectra are photographed in a large spectrograph KSA-1 with three-lens illumination and a two-step filter on the slit, with 1 min. sparking and 2 min. exposure. The condensed spark discharge is set up with a current strength of 1·8 amp., analytical gap 2·5 mm, secondary gap 3 mm, capacitance 0·01 μF and self-inductance 0·01 mH. The spectrograph slit is 0·02 mm wide; the plates are "spectral" type 2 of sensitivity 16 GOST units for the short-wave region, and type 1 of sensitivity 0·7 GOST unit for the long-wave region. The analysis is carried out from a calibration curve with a determination of the plate contrast for each analytical line-pair of each spectrum by photometry of two orders of one of the analytical lines. The reproducibility of the results is given by $\sigma = 80\,R/b$, where R is the mean range of variation in $\triangle S/\gamma$ units, b is the tangent of the angle of slope of the curve, and σ is the relative error (%) with three-fold photography of the spectra. The value of σ varies from 2·1% to 6·7%, according to the element being determined. The analytical line-pairs in A and the concn. range in % (in brackets) are: Ni 2416 and Fe 2417·8 (1 to 25); Ni 2437 and Fe 2440·4 (2 to 25); Ni 3012 and Fe 3009·5 (2 to 25); Cr 2792 and Fe 2793·8 (1 to 32); Cr 2860 and Fe 2828·6 (1 to 32); Cr 3128 and Fe 3154·2 (1 to 32); Mo 2816 and Fe 2828·6 (0·2 to 4·0); Mn 2576 and Fe 2577·9 (0·2 to 1·0); Mn 2933 and Fe 2966·5 (0·2 to 2·0); Ti 3075 and Fe 3062·2 (0·03 to 1·0); Si 2881 and Fe 2883·7 (0·2 to 2·0); V 2908 and Fe 2926·5 (0·15 to 3·0); V 3063 and Fe 3062·2 (0·2 to 3·0); V 3102 and Fe 3062·2 (0·2 to 3·0); W 2397 and Fe 2396·7 (from 1·2); and Co 2580 and Fe 2574·3 (1 to 4).

II. Calculation of the diluting effect of third elements. E. L. Grinzaid and F. D. Korobko. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 91–101; *Ref. Zhur., Khim.*, 1960, (1), Abstr. No. 876.—Methods for removing or allowing for the influence of third elements and their diluting effect on the base element of the alloy are discussed. By the procedure described above, the spectra of many standard steels are photographed to establish the calibration curves of log (I_1/I_0) *vs.* log (C/C_0), where C_0 is the concn. of Fe in the steel. It is shown that when constructing curves on these co-ordinates, a single curve is obtained for all steels with high concn. of Ni and Cr and of W and Mo. It is not possible to obtain a single curve for Mn, Ti and Si. It is concluded that the positions on the curves of points for Mn, Ti and Si depend not only on the concn. of Fe, but also on other factors which have not been taken into account. A weakening of the lines due to Fe, which is not always proportional to the change in the concn. of Fe, is observed on passing from low- to high-alloy steel. C. D. KOPKIN

3748. **Determination of boron in steel.** B. Kysil and J. Vobora (Chem. Lab. SONP, Kladno, Czechoslovakia). *Coll. Czech. Chem. Commun.*,

1959, **24** (12), 3893–3902 (in German).—The colorimetric method with quinalizarin (up to 0·2% of B) and a potentiometric method (0·2 to 5% of B) are recommended. For each type of steel a suitable procedure must be chosen. In the presence of interfering elements a preliminary separation of B by distillation, electrolysis or by means of ion exchangers is recommended. *Procedure for Ti- and V-free steel, sol. in H_2SO_4, and containing up to 0·2% of B*—Dissolve the sample (1 g) in a mixture of H_2O (4·5 ml) and conc. H_2SO_4 (1·5 ml) and filter off the undissolved residue; to the filtrate in an electrolysis vessel add $NaKCO_3$ (0·5 g) and electrolyse; dilute the soln. to 10 ml and to 2·5 ml add Na_2SO_3 (0·05 g) and quinalizarin soln. (0·01 g in 1 litre of H_2SO_4, *d* 1·824) (20 ml), cool, and measure the extinction at 572 to 600 mμ. Transfer the undissolved residue with the filter to a platinum crucible, ignite, then fuse the residue with $NaKCO_3$ (0·5 g). Dissolve the melt in a small vol. of H_2O, add conc. H_2SO_4 (1·5 ml), dilute with H_2O to 10 ml, mix and proceed as described above. To determine B in steel containing Ti, V and W, dissolve the sample in a mixture of H_2SO_4 and H_3PO_4 or after fusion with Na_2O_2, and separate B by distillation with methanol. *Procedure for steel sol. in HCl, containing 0·2 to 5% of B*—To the sample (1 to 2 g) add HCl (1:2) (15 to 30 ml) and dissolve by heating under reflux. Oxidise the soln. with H_2O_2 (15 to 25 ml), remove the excess of H_2O_2 by boiling, filter, dilute the filtrate with H_2O, adjust to pH 2 and pass it through a cation exchanger (Na^+ form) (3 ml per min.), wash the column with H_2O, heat the soln. under reflux, cool, adjust to pH 4, add mannitol or fructose and titrate potentiometrically with 0·1 *N* NaOH to pH 9. Steel insol. in HCl is decomposed by fusion with Na_2O_2. J. ZÝKA

3749. **Determination of boron in iron and low-alloy steels with 1:1′-dianthrimide: a colorimetric method that does not require preliminary separations.** L. Danielsson (Swedish Inst. for Metal Research, Stockholm). *Talanta*, 1959, **3** (2), 203–207 (in English).—A procedure is described for the determination of B in concn. down to 0·001%. The steel is dissolved in 2 *M* H_2SO_4 and filtered. Both filtrate and residue contain B. The filter is ignited and the residue is fused with Na_2CO_3. The melt is dissolved in 2 *M* H_2SO_4 and H_2SO_3 is added to reduce oxidising ions. After addition of 96% H_2SO_4, B is determined spectrophotometrically in both soln. with 1:1′-dianthrimide (*cf. Anal. Abstr.*, 1960, **7**, 3656). With a final H_2SO_4 concn. of 90%, Fe remains in soln. and does not interfere. Vanadium interferes and can be removed by ion exchange. The results agree well with the certified values of N.B.S. steels. G. BURGER

3750. **Spectrochemical determination of aluminium in chromium - nickel austenitic steel and seam welds.** E. S. Kudelya. *Avtomat. Svarka*, 1959, (6), 28–30; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4614.—The spectra are excited in a Tesla spark discharge as previously described. The Al is volatilised from the sparked layer by the action of the spark, but the value of $\triangle S$ for the lines Al 3082·1 and Fe 3083·7 A becomes stabilised after a three-minute sparking because of a reduction in the intensity of the Fe line. The slope of the calibration curves is reduced by this procedure, so that the preliminary sparking is carried out for only 50 sec., which allows other elements also to be determined in seam welds. The error for 0·25 to 1·8% of Al is ± 4%. By using standard chromium - nickel austenitic steels Nos. 5, 25, 123, and 124, and steels KhMYuA Nos. 102, 103 and 104 of the Urals Inst. of Metals, it is shown that Al may also be determined by the absolute blackening of the line; the accuracy is not less than in the procedure using $\triangle S$ values. In the absence of preliminary sparking the shape of the calibration curves is independent of the type of steel. C. D. KOPKIN

3751. **Use of gelatin in the determination of silicon in complex steels.** M. I. Karmanova. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 40–41; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4681.—Silica is dehydrated with H_2SO_4 in the presence of H_3PO_4, with subsequent coagulation with gelatin soln. *Procedure*—Dissolve the sample (1 g for samples containing > 0·5% of SiO_2, or 2 to 4 g for 0·15 to 0·5%) in 50 to 100 ml of a mixture of 600 ml of water, 120 ml of conc. H_2SO_4 and 100 ml of H_3PO_4 (sp. gr. 1·7). If the sample does not dissolve in this, dissolve it in aqua regia or HCl and add H_2SO_4 and H_3PO_4. Add dil. HNO_3 to oxidise Fe^{2+}, and evaporate on a sand bath until crystallisation begins; cool, and add 10 to 20 ml of HCl (1:1) and a little water to dissolve the salts completely. Add 1 ml of a 1% gelatin soln. at a temp. ⩾ 50°, stir vigorously, and set aside for 1 to 2 min.; then add a further 2 ml of gelatin soln., stir, set aside in the dark for 10 to 15 min., dilute with hot water to 50 or 60 ml, add paper pulp and filter. Wash the ppt. of silicic acid with hot water, then with dil. HCl, and then again with water till the washings are free from Cl^-; ignite, weigh, and treat with HF in the usual way to determine impurities (< 0·5 mg). The method is simple and gives accurate results. C. D. KOPKIN

3752. **Gravimetric determination of lead in iron and steel (lead content > 0·05%).** B.I.S.R.A. Methods of Analysis Committee. *J. Iron St. Inst.*, 1959, **193** (4), 350–353.—The recommended method is based on the pptn. of Pb as sulphide from aq. HCl, followed by dissolution in HNO_3 and conversion into the molybdate. The method is applicable to carbon and leaded steels containing Cu, Cr, Mo or Ni, but ⩾ 0·25% of Sn or ⩾ 2% of W. A reproducibility of 0·01% for concn. of 0·2% of Pb is claimed. For Pb contents < 0·05% the method is not sufficiently reproducible. It is suggested that when the ppt. of lead molybdate is discoloured because of traces of Fe, a second pptn. be made after treatment of the ppt. with HNO_3 and tartaric acid. J. W. O. PYEMONT

3753. **Separation and determination of titanium in stainless steels.** M. N. Nadkarni, G. G. Nair and C. Venkateswarlu (Anal. Div., Atomic Energy Estab., Trombay, Bombay, India). *Anal. Chim. Acta*, 1959, **21** (6), 511–514 (in English).—After ether extraction of Fe^{III} from the acid soln. (6 *N* with respect to HCl) of the sample (0·1 g), Ti is co-pptd. with Zr as phosphate from the 2 to 3 *N* acid soln., filtered off, digested with NaOH, and re-filtered. The residue of sodium titanate and zirconate is dissolved in H_2SO_4 before a spectrophotometric determination by the H_2O_2 method. T. R. ANDREW

3754. **Determination of nitrogen in steels of various compositions.** K. A. Sukhenko, P. P. Galonov and T. V. Barasheva. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1959, **23** (9), 1123–1126; *Ref. Zhur., Khim.*, 1960, (6), Abstr. No. 22,100.—In the preparation of standards, nitrogen, as nitrided ferrochrome, is added

to stainless steel during smelting; a less satisfactory standard can be made without the addition of nitrogen by smelting in a vacuum furnace. The concn. of N in the standard (0·02 to 0·19%) is checked by chemical methods. Spectra are excited by a low-voltage spark discharge of 300 μF capacity with two burnings per half-cycle and a 1-sec. exposure, controlled by a timing relay. The spectra are photographed on type 3 spectrographic plates (sensitivity 16 GOST units) with a hemispherical tungsten counter-electrode and a spark gap of 0·3 mm. The electrodes are enclosed in a chamber; the discharge is carried out in an atmosphere of He at a pressure of 700 torr. The calibration curve of $\triangle S$ *vs.* log C for the 3994·99-A nitrogen line is linear. The basal soln. is used as the comparison sample. An analysis of the results demonstrates the influence of group-III elements.

K. R. C.

3755. **Determination of phosphorus in vanadium steel.** Katsumi Aiba (Shinhokoku Iron and Steel Co., Shinjuku, Kawasaki). *Japan Analyst*, 1959, **8** (7), 436–440.—The extraction of molybdophosphate with a mixture of amyl and ethyl acetates (7:3) was used for the preliminary separation of P from vanadium steel, the V being reduced with Na_2SO_3. By using two 10-ml portions of solvent mixture, the extraction is quantitative. There is no interference from $<$ 4 mg of As or $<$ 250 mg of V; Cr is removed as CrO_2Cl_2 and W as WO_3. *Procedure*—Dissolve the sample (1 g) in a mixture of HNO_3 and HCl (1:1) (30 ml), heat to white fumes with $HClO_4$ (15 ml), cool, boil with $HClO_4$ (10 ml), water (20 ml) and Na_2SO_3 soln. (5%) (10 ml) for 2 min., then expel SO_2 and filter. Dilute the filtrate to 100 ml with ammonium molybdate soln. (1%) (20 ml), shake with the acetate mixture (20 ml) and evaporate the org. layer to dryness. Dissolve the residue in aq. NH_3 soln., add HNO_3, and precipitate ammonium molybdophosphate by the usual method.

K. Saito

3756. **Determination of small amounts of phosphorus, calcium, magnesium and copper in complex steels.** A. S. Andreev and N. A. Pospelova. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 56–76; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4713.—To determine P, treat a soln. of the sample with H_2O_2 and a slight excess of aq. NH_3, separate the hydroxide ppt. containing the P, convert P into ammonium molybdophosphate, and dissolve the latter in aq. NH_3. To the soln. add acetic acid, ammonium acetate and ammonium citrate (**I**) or EDTA (disodium salt) (**II**); heat, add 8-hydroxyquinoline, wash the pptd. molybdenum hydroxyquinolinate with water, dry it at 130° to 140° and weigh. Determine Cu photometrically with Na diethyldithiocarbamate, extracting the complex with CCl_4 from a soln. (pH 9 to 11) containing **I** or **II**. In determining Ca and Mg, first separate them from interfering elements and then determine Ca by titration with 0·01 *M* **II** with murexide as indicator, and Mg photometrically with Titan yellow. Calcium and Mg are separated from other elements by precipitating them by means of KOH soln. in the presence of H_2O_2 and K_2CO_3 (separation from W, Mo, V, P, Al, Si, Nb, Ti and Zr), or by pptn. with ammonium phosphate in ammoniacal medium (separation from Ni, Co, W, V, Mo and Cr), or by extraction of the pyridine - thiocyanate complexes of Fe, Ni, Co and Mn with $CHCl_3$. Iron may be removed by extraction with amyl acetate from 6 *N* HCl.

C. D. Kopkin

3757. **Determination of sulphur in cast iron. A study of the combustion method with an assessment of the value of vanadium pentoxide as flux.** H. Green. *Metallurgia, Manchr.*, 1959, **60** (361), 229–232.—The possible sources of error are discussed and a comparison is made between three types of flux. To obtain stoicheiometric recovery some means of absorbing the SO_3 formed during the combustion is necessary, and the determination must be completed by an alkalimetric titration; V_2O_5 would then be a suitable flux.

J. W. O. Pyemont

3758. **Colorimetric determination of small amounts of sulphur in steel and in pure iron and cobalt.** P. Tyou and L. Humblet (Centre National de Recherches Métall., Abbaye du Val-Benoit, Liège, Belgium). *Talanta*, 1960, **3** (3), 232–239 (in French).—From 0·001 to 0·02% of S in steel, iron or cobalt can de determined by converting it into H_2S which, after absorption in alkaline zinc acetate soln., is allowed to react with NN-dimethyl-*p*-phenylenediamine and $FeCl_3$ to form methylene blue. The extinction of the blue colour is measured (after 15 to 45 min.) at 650 mμ in a 2-cm cell with slit-width $\simeq$ 2 mμ. As Beer's law is not followed, a special calibration curve (based on a sample of K_2SO_4) is required for the range of 0 to 120 μg of S per 100 ml. A sample of steel or iron is attacked with conc. HCl and the sulphide sulphur is determined; any oxidised S in the residual liquid is then reduced with a mixture of HI and H_3PO_2 and the H_2S formed is determined separately. A sample of cobalt is dissolved in conc. HNO_3, the excess of which is removed by evaporation almost to dryness with HCl; the SO_4^{2-} are reduced to H_2S with HI and H_3PO_2 and the usual procedure is then followed. Provided that certain precautions are taken in the analyses, the results agree well with those obtained by the usual standard methods.

W. J. Baker

3759. **Comparative evaluation of methods for the determination of selenium in chromium - nickel steel.** A. S. Andreev. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 24–34; *Ref. Zhur., Khim.*, 1960, (2), Abstr. No. 4697.—The following four methods are studied—(*i*) distillation of Se with HBr with subsequent gravimetric or photometric determination; (*ii*) separation by reduction with $SnCl_2$ in HCl - H_2SO_4 soln. with subsequent determination as above; (*iii*) determination by the method of Tananaev and Murashova (*Zhur. Anal. Khim.*, 1948, **3**, 3); (*iv*) direct determination of H_2SeO_3 by potentiometric titration with $KMnO_4$ soln. or visual titration with N-phenylanthranilic acid as indicator. The disadvantage of (*i*) is that large amounts of Br and HBr are required; (*ii*) is inconvenient because Se separates in a microcrystalline state from soln. containing large amounts of H_2SO_4 and sulphates, which causes large losses on filtration; (*iii*) gives low results, but it may be used if weak oxidants (*e.g.*, Fe^{3+}) are added when the sample is being dissolved; (*iv*) is recommended for the analysis of simple and alloyed steels in works laboratories. Satisfactory results were obtained in the determination of Se in a sample of chromium - nickel steel of type 18-8 by these methods. Slight deviations from the mean Se content are due more to the non-homogeneity of the sample than to the method used.

C. D. Kopkin

3760. **Spectrophotometric determination of molybdenum in steel with 3:5:7:3′:4′-pentahydroxyflavanone (dihydroquercetin).** F. L. Chan and R. W.

Moshier (Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, U.S.A.). *Talanta*, 1960, **3** (3), 272–276.—The method is based on the formation of a stable yellow complex of Mo with 3:5:7:3′:4′-pentahydroxyflavanone (**I**) at pH 5. The sample (≡ 1 to 2 mg of Mo) is dissolved in 50% HCl and conc. HNO_3 under conditions such that any Cr and V remain present as Cr^{III} and V^{IV}. The Mo in the dil. HCl is then extracted (in five stages) with a 0·1% soln. of benzoin α-oxime in $CHCl_3$. To the entire organic extract (a suspension) is added 1 ml of 5% NaOH in methanol, followed, after shaking, by absolute ethanol until the vol. is 100 ml. This clear soln. (5 ml) plus 0·5 ml of water is then added to the acetate buffer (pH 5) (0·5 ml) and 3 ml of a 0·3% soln. of **I** in ethanol. The mixture is well stirred, diluted to 10 ml with ethanol and the max. extinction is measured at 410 mμ after ≮ 10 min. Provided that a sufficient excess of **I** is present, Beer's law is followed by 5 to 100 μg of Mo in 10 ml. Tungsten, Cr and V are partly extracted by benzoin α-oxime; Cr and V do not interfere, but if W is present the Mo should be separated from it by pptn. as MoS_3. For contents of Mo of 0·035 and 1·01%, respectively, the error is −0·0013 and ±0·014%. W. J. BAKER

3761. **Some problems in determination of manganese in steel.** M. Z. de Lippa. *J. Iron St. Inst.*, 1960, **194** (1), 54–62.—Factors that affect this determination were investigated, including the selection of line pairs, excitation conditions and polarity. The influence of C, S, P, Cr and Al is reported, and the importance of the size, preparation and prior history of the sample is considered. J. W. O. PYEMONT

3762. **Determination of nickel and cobalt in high-alloy and stainless steels.** L. L. Lewis and W. A. Straub (Appl. Res. Lab., U.S. Steel Corp., Monroeville, Pa.). *Anal. Chem.*, 1960, **32** (1), 96–99.—After separation from other constituents by anion exchange of the chloro complexes, followed, for Ni, by pptn. with dimethylglyoxime, Ni and Co are titrated with EDTA (disodium salt) soln. Results for Co (5 to 40%) are within 0·1% of agreed values and results for Ni (0·1 to 20%) are also in good agreement. T. R. ANDREW

3763. **2:4-Dinitrophenylhydrazone of diacetyl monoxime: a new sensitive reagent for cobalt.** V. D. Anand and G. S. Deshmukh (Chem. Dept., Hindu Univ., Benares, India). *Naturwissenschaften*, 1959, **46** (23), 648 (in English).—Mix the test soln. (1 drop) with conc. aq. NH_3 (2 drops) and a 0·05% ethanolic soln. of the reagent (prep. described) (2 drops), add NH_4Cl and remove excess of the reagent by shaking with diethyl ether. A light to deep red colour develops according to the amount of Co. The lighter colour produced by Cu and Ni is destroyed by the addition of KCN soln.; Ag and Pd do not react. The limits of dilution and detection for Co are 1 in 5×10^5 and 0·1 μg, respectively. A. R. ROGERS

3764. **Macro- and micro-determination of traces of cobalt. IV. Separation by ion exchange: losses and contamination in the course of analytical operations.** J. Vogel, D. Monnier, W. Haerdi and P. E. Wenger (Lab. Chim. Minérale, Univ. Genève). *Helv. Chim. Acta*, 1960, **43** (1), 217–229 (in French).—For the determination of 0·01 to 1 μg of Co, a soln. is suitably prepared, interfering cations such as Fe are extracted with chloroethane, and the Co is adsorbed on a Dowex 1-X8 column. It is subsequently eluted with an ether soln. of dithizone, the complex is decomposed and the Co is determined spectrophotometrically or polarographically. About 84% of the Co initially present is recovered. J. L. PROSSER

3765. **Determination of cobalt as tellurite.** V. D. Anand and G. S. Deshmukh (Chem. Dept., Hindu Univ., Benares, India). *Z. anal. Chem.*, 1960, **172** (4), 264–268 (in English).—*Procedure*—To the Co soln. (containing 0·001 to 0·12 g of Co) add a measured excess of 0·5 *M* K_2TeO_3 and KCl (1 to 2 g). After 2 hr. filter off the pptd. $CoTeO_3.H_2O$, wash with warm H_2O, dry at 250° for 4 to 6 hr. and weigh. Alternatively, treat the filtrate with an excess of 0·1 *N* $K_2Cr_2O_7$, followed by an excess of standard $(NH_4)_2SO_4.FeSO_4$ soln., and back-titrate the excess of Fe^{2+} with 0·1 *N* $K_2Cr_2O_7$, with ferroin as indicator. Both methods have accuracies of ≃ 0·3% at high and ≃ 1% at low concn. J. P. STERN

3766. **Conductimetric and pH studies on cobalt tellurite.** G. S. Deshmukh, V. D. Anand and A. K. Vishwanath (Chem. Dept., Hindu Univ., Benares, India). *Z. anal. Chem.*, 1960, **172** (4), 260–264 (in English).—Conductimetric (direct and reverse) and pH titration curves for aq. $CoCl_2$ soln. (0·001 to 0·1 *M*) with aq. K_2TeO_3 soln. (0·001 to 0·5 *M*) show sharp inflections at a molar ratio of 1:1. The addition of ethanol up to 50% causes a decrease in the sharpness of the inflection in the conductimetric curve. J. P. STERN

3767. **Catalytic determination of micro amounts of cobalt in the presence of zinc.** J. Laszlovszky (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1960, (1), 72–78 (in German).—Cobalt in the concn. range 10^{-2} to 10^{-5} μg in 1 ml of soln. catalyses the oxidation of alizarin by sodium perborate at 90°. The reaction time is determined by the visual detection of a yellow coloration. *Procedure*—Into a test-tube place 0·03% alizarin soln. in ethanol (1 ml), water (2 ml), sample soln. (1 ml) and satd. sodium perborate soln. (1 ml), mix and place in a thermostatically controlled vessel at 90° ± 0·1°. Measure the time required for the soln. to change from violet to yellow, with a previously oxidised alizarin soln. as standard. The concn. of Co can be read off from a previously prepared graph. If more than 50 μg of Zn is present, a series of dilutions of the sample soln. are analysed and the concn. of Co is calculated by reference to a graph. W. T. CARTER

3768. **Photometric determination of cobalt in nickel alloys and steel.** K. L. Cheng and F. J. Warmuth (Metals Div., Kelsey-Hayes Co., New Hartford, N.Y., U.S.A.). *Chemist Analyst*, 1959, **48** (4), 96–97.—A modification of the method of Cheng (*Anal. Abstr.*, 1958, **5**, 4133) is described which overcomes the interference due to alloying metals by separating Co on an anion-exchange resin. The Co is then converted into a purple complex with nitrilotriacetic acid and sodium perborate, and determined photometrically at 560 mμ. G. S. ROBERTS

3769. **Application of EDTA to the titrimetric determination of nickel in non-ferrous alloys.** V. A. Nelson and L. J. Wrangell (Res. Lab., Allis-Chalmers Mfg. Co., Milwaukee, Wis., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 99–103.—Nickel is separated by a double pptn. with dimethylglyoxime,

the ppt. is dissolved in HCl, the soln. is evaporated to 2 ml, then diluted to about 50 ml and, after addition of 5 ml of aq. NH_3 (sp. gr. 0·94), titrated with EDTA (disodium salt) soln. Cal Ver I [murexide - NaCl (1:500)] is recommended as indicator. The method has been applied to alloys containing from 0·04 to 66% of Ni.

T. R. ANDREW

3770. **New spot test for palladium.** Buddhadev Sen (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (1), 22–24 (in English).—*Procedure*—Place 1 drop of the neutral or acid test soln. in a spot-plate depression and add 1 drop of a 1% soln. of phenyl 2-pyridyl ketoxime in 95% ethanol. If the soln. is strongly acid add a few drops of 0·5 *M* Na_2CO_3 after the reagent soln. A yellow colour is obtained in the presence of 1 μg or more of Pd^{2+}. If Hg^{+}, Hg^{2+}, CrO_4^{2-}, MnO_4^{-}, $[Fe(CN)_6]^{3-}$ or another metal of the platinum group is present, treat 1 drop of the weakly acid soln. of Pd^{2+} with 1 drop of the reagent soln. and 10 drops of water, add 0·5 to 1 ml of $CHCl_3$, mix, and allow to separate. The $CHCl_3$ is coloured yellow if 0·5 μg or more of Pd^{2+} is present. When Cu^{2+}, Fe^{3+}, Co^{2+} or Ni^{2+} are present, add 10 drops of 0·1 *M* EDTA (disodium salt) and 1 drop of the reagent soln. and extract the complex of Pd with $CHCl_3$. If Au^{3+} are present, add 1 drop of the reagent soln., 10 drops of water, a few drops of 0·5 *M* Na_2CO_3 and a little ascorbic acid, warm to reduce the Au^{3+} to the metal and extract with $CHCl_3$. Most other common ions are without effect on the procedure first described.

H. N. S.

3771. **Determination of palladium by $\alpha\beta$-dioximinoacetoacet-o-chlor[o]anilide [$\alpha\beta$-dioximinobutyro-o-chloroanilide].** J. S. Dave and A. M. Talati (Textile Chem. Dept., M.S. Univ., Baroda, India). *J. Indian Chem. Soc.*, 1959, **36** (12), 838–840.—Palladium (8 to 20 mg in $\simeq$ 200 ml of dil. HCl soln.) is pptd. quant. at $\simeq$ 60° and pH 0·4 to 0·7 by the addition of a slight excess of $\alpha\beta$-dioximinobutyro-*o*-chloroanilide (1% ethanolic soln.). The ppt. is digested on the water bath for $\simeq$ 1 hr., collected, washed with dil. HCl and then water, and dried to constant wt. (as $PdC_{20}H_{18}N_4O_4Cl_2$) at 110° to 120°. The determination can be made in the presence of most common metal ions, but NO_3^{-} interfere even when the pptn. is made from an alkaline soln. The error is usually within +0·1 mg; pptn. is quant. up to pH 10.

W. J. BAKER

3772. **Determination of platinum, sulphur and chlorine in platinum reforming catalysts.** A. L. Conrad and J. K. Evans [Res. Dept., The Standard Oil Co. (Ohio), Cleveland, U.S.A.]. *Anal. Chem.*, 1960, **32** (1), 46–49.—The sample (0·1 g) is mixed with 0·4 g of $AlCl_3$, in a ceramic crucible; $\simeq$ 0·6 g of $AlCl_3$, $\simeq$ 0·25 g of Al_2O_3 and $\simeq$ 1 g of iron (3:1:3, by vol.) are added and the mixture is ignited in an induction furnace, the issuing vapours being absorbed in 110 ml of HCl (1:10). The absorbent soln. is shaken with cupferron in $CHCl_3$ to remove Fe, and Pt is determined photometrically with NN-dimethyl-*p*-nitrosoaniline at 525 mμ. The interference of volatile platinum salts in combustion methods for Cl and S can be eliminated by bubbling the issuing gases through boiling formic acid. Sulphur dioxide is not absorbed, Pt is pptd. as platinum black and, if a standard $AgNO_3$ soln. is added to the formic acid, AgCl is pptd. during the combustion, and the excess of $AgNO_3$ may be subsequently titrated.

T. R. ANDREW

3773. **Potentiometric titration of sodium clay minerals.** A. Buzágh and F. Szántó (Inst. Colloid Chem. and Technol., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1960, **66** (1), 13–16.—The potentiometric titration of sodium clay minerals is carried out on a 0·5 to 0·8% suspension with 0·01 *N* HCl, by means of a pH meter and a glass electrode. The curves show two inflections in the case of montmorillonite-type minerals: the first corresponds to the neutralisation of free Na_2CO_3 or OH^{-}, and the second to the complete ion exchange of the mineral. The ion-exchange capacity (acid equivalent) of the mineral is given by the difference between the milli-equiv. of acid used at the two inflections. Finely dispersed $Al(OH)_3$ or $Fe(OH)_3$ and suspended $CaCO_3$ interfere. The titration can also be carried out by using phenolphthalein and methyl red to indicate the end-points, but the equiv. obtained by this method is 10% less than that obtained potentiometrically. The speed of titration affects the result, and a 1 to 2% accuracy can be achieved by slow ("equilibrium") titration. In this, after a preliminary titration, add increasing volumes of 0·01 *N* HCl to twenty 20-ml aliquots of suspension, each containing a known wt. of dry material. Add phenolphthalein and then methyl red to each sample tube. After repeated mixing, keep the mixtures overnight; the position at which the strong pink of methyl red appears corresponds to the potentiometric end-point. These methods have the advantage that the ion-exchange capacity can be determined directly, in the most dispersed state of the sample, without conversion into the hydrogen form. The prep. of sodium clay minerals from natural calcium bentonite is also described.

A. G. PETO

3774. **Quantitative solution spectral analysis of macro components of bauxite.** M. Kriváň and M. Matherny (Dept. of Phys. Chem., Sch. of Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1959, **13** (12), 796–802.—A method for the determination of Al_2O_3, Fe_2O_3, SiO_2 and TiO_2 with a rotating disc as carrier electrode was developed. The sample is fused with a 10-fold excess of a mixture of Na_2CO_3 and $Na_2B_4O_7$ (1:1·85), and the melt is dissolved in citric acid buffered with Na citrate to prevent the formation of SiO_2. Nickel is used as internal standard. The results are referred to calibration curves. The following accuracies were achieved— $\pm$ 1·34% for Al_2O_3, $\pm$ 2·3% for Fe_2O_3, $\pm$ 3·1% for SiO_2 and $\pm$ 4·7% for TiO_2.

J. ZÝKA

3775. **Rational analysis of magnetite, pyrite and chalcopyrite in sulphide ores with a Geiger-counter X-ray diffractometer.** Shizo Hirano and Hiroo Sasuga (Inst. Tech.-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1959, **8** (8), 495–500.—Magnetite (4 to 85%) (**I**), pyrite (30 to 90%) (**II**) and chalcopyrite (6 to 20%) (**III**) in cinder and tailings are satisfactorily determined diffractometrically (25 kV, 8 mA; scanning rate, 0·25° per min.) with CoK_α radiation, with rock salt as internal standard. Reproducibility of the diffracted lines decreases with increase in grain size. Pulverisation to several microns suffices for **I** and **II**, but to < 1 micron is required for **III**.

K. SAITO

3776. [**Determination of**] **scandium, chromium and europium in stone meteorites by simultaneous neutron activation analysis.** G. L. Bate, H. A. Potratz and J. R. Huizenga (Argonne Nat. Lab., Lemont, Ill.). *Geochim. et Cosmoch. Acta*, 1960, **18** (1–2), 101–107.—The preparation of the samples and their

activation is as described for the determination of Th (*Anal. Abstr.*, 1959, **6**, 4720). Details are here given of the radiochemical separation procedures for Sc, Cr and Eu. The method involves separate flux monitors for each element during activation, but the simultaneous multiple element assay is especially appropriate for meteorite analysis in view of the limited amount of material available.

R. A. HOWIE

3777. **Chemical determination of sodium and potassium in raw materials and clinker in cement works.** L. Burglen and P. Longuet (Cent. d'Étud. et de Recherches de l'Ind. des Liants Hydraul., Paris). *Rev. Matér. Constr., C*, 1959, (530), 257–265.—The sample (0·5 to 1 g) is decomposed with HCl, or a mixture of HF, H_2SO_4 and H_3BO_3, or of $CaCO_3$ and NH_4Cl (Lawrence Smith method). The SiO_2 and mixed hydroxides are pptd. from the soln. (buffered with $CaCO_3$) and the alkali metals are then determined in the filtrate. Sodium is pptd. with zinc uranyl acetate (**I**) and its amount is calculated from the content of UO_2 in the ppt. (determined by reduction of U^{4+} to U^{3+} in a Jones reductor and with aeration, followed by cerimetric titration in an inert atmosphere). Potassium is determined gravimetrically, in another aliquot, as K tetraphenylboron in 0·1 *N* HCl soln., or volumetrically (as described) after dissolution of the ppt. in acetone. Refractory samples must be fused at $\simeq$ 775° for 45 min. with a mixture of anhyd. $BaCl_2$ and anhyd. $Ba(OH)_2$ (1 : 5) in a nickel or steel crucible. The bulk of the Ba in the aq. extract is removed as $BaCO_3$, and the remainder by boiling the filtered soln. with powdered gypsum (1 g); Na and K can then be determined in the final filtrate. The reproducibility is $\simeq$ 0·01% for Na_2O and $\simeq$ 0·02% for K_2O for a given method of sample attack. Lithium interferes with the determination of Na by co-formation of a more sol. double salt with **I**, but is usually present only in high-alumina cements and bauxites. It must be removed and determined separately (with **I**) by a triple extraction of the fusion-cake with boiling 2-ethylhexanol, followed by evaporation to dryness of the combined extracts. A procedure for the recovery of U (as uranyl acetate dihydrate) from a large vol. of wash liquids is described.

W. J. BAKER

3778. **Modern methods of slag analysis.** W. E. Clarke (Chem. Lab., B.C.I.R.A., Alvechurch, Birmingham, England). *J. Res. Brit. Cast Iron Ass.*, 1959, **7** (15), 867–884.—The classical methods of slag analysis and their deficiencies are discussed. New methods aimed at increasing the speed, reducing the amount of skill required and avoiding hidden errors in the summation of results are described. These include the use of a spectrophotometer or a filter-type absorptiometer for determining Fe, Mn, and Ti; the use of a filter-type flame photometer for determining alkali metals; the use of volumetric methods that do not require preliminary separations; solvent extraction rather than precipitation for separations; and the avoidance of errors in summation by making each determination on a separate sample or aliquot so that difference results are avoided. An analytical scheme is given and details of the methods are presented.

C. H. COWPER-COLES

See also Abstracts—**3597**, Metallurgical spectroscopy. **3601**, *o*-Halogeno-*o'*-hydroxyazo compounds of Ca, Mg and Th. **3602**, Separation of Zn-group sulphides. **3603**, Brucine as redox indicator for Fe^{2+} and U^{4+}. **3607**, Titrations with $K_4Fe(CN)_6$. **3825**, Titration of Ag and Cu. **3844**, Water in various materials. **4017**, Reagent for NO_3. **4046**, Determination of O in gases. **4056**, Chromatography of inorg. ions. **4059**, Water in gases. **4075**, Spectrographic determination of Ti and Be.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

3779. **Micro-elementary analysis.** H. Malissa (Max Planck Inst. für Eisenforschung, Düsseldorf, Germany). *Mikrochim. Acta*, 1960, (1), 127–144 (in German).—In a rapid method for the determination of C, H and S, the sample is burnt in pure oxygen in an empty tube, the products of combustion are absorbed in suitable soln. and determined by conductivity measurement. Carbon dioxide is absorbed in 0·005 *N* NaOH, interference from SO_2 being eliminated by a guard-tube filled with ion-exchange resin. Water is converted into acetylene by passage through a tube packed with CaC_2 and the acetylene is burnt to CO_2, which is determined as already described. Sulphur dioxide is absorbed in 0·004 *N* $TlCl_3$ adjusted to pH 3 with HCl. The elaborate apparatus required is only briefly described. An analysis can be completed in 10 min.

W. T. CARTER

3780. **Determination of carbon in organic substances by an oxygen-flask method.** R. S. Juvet and Jen Chiu (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 130–131.—A sample (3 to 25 mg) is placed on a glass-wool pad in a special flask and ignited electrically in an atmosphere of O. The CO_2 evolved is absorbed in carbonate-free 0·5 *N* NaOH and the soln. is titrated with 0·1 *N* HCl to the methyl orange end-point. A detailed description of the apparatus and procedure is given. A complete determination can be carried out in 20 min. and no expensive apparatus is required. Results for a variety of compounds show a mean absolute error of 0·3%. Unsatisfactory results were observed for halogen compounds and Na oxalate.

S. M. MARSH

3781. **Quantitative organic analysis. XXII. New method for a rapid automatic combustion of organic substances. Micro-determination of carbon and hydrogen.** M. Večeřa, F. Vojtěch and L. Synek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 93–100.—Solid and liquid substances can be burnt within 3 to 8 min. with the use of a new method based on the stepwise switching on of the combustion zones. The substance is placed in a long, narrow platinum vessel, protected by a quartz tube. Liquid samples are burnt in a capillary tube. Good results were obtained in the micro-determination of C and H in the presence of Co_3O_4. Detailed drawings of the apparatus are given.

J. ZÝKA

3782. **Simultaneous determination of carbon, hydrogen, sulphur and halogens.** V. A. Klimova and G. K. Mukhina (Inst. Org. Chem., Acad. Sci.,

Moscow). *Izv. Akad. Nauk SSSR*, 1959, (12), 2248–2250.—A method for the analysis of organic substances makes use of the fact that Co_3O_4 heated between 400° and 500° absorbs sulphur oxides and not halogens. The organic substance is burnt in a stream of oxygen in a combustion tube containing platinum foil heated at 900° to 950°, and boats containing electrolytically pptd. Ag and Co_3O_4. The H_2O and CO_2 formed are absorbed on anhydrone and Ascarite and the halogens on Ag heated at 420°. The sulphur oxides are absorbed on Co_3O_4 heated at 470° to 500° for substances containing Cl or I, or at 410° to 430° for those containing Br. The sulphur oxides are extracted from the Co_3O_4 with H_2O and titrated against $Ba(NO_3)_2$. Phosphorus and Si do not interfere and can be determined in the ash. A. BURWOOD-SMITH

3783. **Gas-proportional counting of carbon-14 and tritium, and the dry combustion of organic compounds.** D. R. Christman and C. M. Paul (Brookhaven National Lab., Upton, L.I., N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 131–132.—An anti-coincidence counter, similar to those used for ^{14}C except that it has no mercury shield, has been installed to improve the precision and lower limit of detection in gas-proportional counting. The construction and performance of the unit are discussed. A significant increase in the background count of units made from recently purchased glassware has been observed. A modified oxygen-supply tube for use in the dry combustion of organic compounds is described, with diagrams. The incoming oxygen stream is divided so that part is introduced from the end of the combustion tube, and the possibility of explosions, due to flash-back of vapour from the sample leaking into the heated zone of the furnace, is avoided. S. M. MARSH

3784. **Combustion of liquids by the Schöniger technique.** R. Bennewitz (Anal. Lab. VEB Fettchemie, Karl Marx Stadt, Germany). *Mikrochim. Acta*, 1960, (1), 54–57 (in German).—Substances with boiling-points > 200° are absorbed on filter-paper and ignited in the recognised manner. Compounds with lower boiling-points are sealed into small thin-walled bulbs which are then wrapped in filter-paper and ignited, the vapour pressure of the liquids being high enough to rupture the bulbs. The technique has an accuracy of ±0·3%, except with compounds containing 80% of halogen, which give widely erratic results. W. T. CARTER

3785. **Determination of hydrogen in hydrocarbons by the use of β-radiation.** M. Přibyl (Military Tech. Acad., Brno, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (11), 576–578.—The intensity of the radiation passing a layer of the sample (liquid hydrocarbon) is measured with an impulse counter in a Geiger - Müller tube. With a 2-g sample, the determination can be completed within 15 to 20 min. with a mean error of ±0·18% of H. The method is suitable for the determination of H in liquid non-volatile hydrocarbons, in particular lubricating oils. J. ZÝKA

3786. **Simplified micro-determination of nitrogen in organic compounds.** J. Léger (Lab. de Chim. Org., École Pratique des Hautes Études, Service de Chim. Org. des Hormones, Collège de France). *Chim. Anal.*, 1960, **42** (1), 24–27.—A simplified procedure for the Dumas determinations of N on the micro or semi-micro scale is described, with a diagram of the apparatus. E. J. H. BIRCH

3787. **Rapid method for nitrogen determination.** H. Trutnovsky (Inst. für organ. u. pharm. Chem., Univ. Graz, Austria). *Mikrochim. Acta*, 1960, (1), 157–159 (in German).—A simplified combustion apparatus is described in which the sample is burnt in pure oxygen or any required oxygen - carbon dioxide mixture. The oxygen is generated by dropping H_2O_2 on to MnO_2, and excess of oxygen is prevented from entering the nitrometer by a guard-tube, 7 cm long, packed with copper powder and heated to 550°. W. T. CARTER

3788. **New simple nitrometer for Dumas nitrogen determination.** Tetsuo Mitsui (Dept. of Agric. Chem., Coll. of Agric., Kyoto Univ., Japan). *Mikrochim. Acta*, 1960, (1), 150–156 (in English).—The principal features of the apparatus are a spring-loaded plastic plug to replace the top stopcock, and a polyethylene reservoir fitted with a one-way valve instead of the normal levelling bottle. The gas volume is read off without levelling, and corrected to atmospheric pressure by means of a correction curve. The absence of rubber and stopcock lubricant reduces frothing and contamination of the potassium hydroxide. W. T. CARTER

3789. **Modifications of Kjeldahl digestion for organic nitrogen.** R. B. Bradstreet (U.S. Testing Co., Inc., Hoboken, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 114–117.—The use of sucrose as an internal reducing agent in place of salicylic acid - thiosulphate is recommended, since lower temp. are required for reduction. The sucrose is added to the H_2SO_4 before the addition of the sample, and the mixture is maintained between 90° and 100° for 1 hr.; 0·1 g of Se and 18 g of K_2SO_4 are then added and the mixture is boiled for 1 hr. after it has become clear. The digest is then distilled in the usual way. Typical results are tabulated for a wide range of organic nitrogen compounds. Improved results for pyridine-ring compounds are obtained by digesting with H_2SO_4 - H_3PO_4. Pyrazolone, phenazone, benzotriazole and aliphatic compounds containing a nitro group attached to a secondary or tertiary C atom cannot be determined. S. M. MARSH

3790. **Determination of nitrogen in some heterocyclic compounds.** I. Čepčianský and L. Chromcová (Dept. Org. Chem. and Technology, Inst. Chem. Technology, Pardubice, Czechoslovakia). *Sb. Věd. Prac., Vysoké Školy Chem.-Technol., Pardubice*, 1959, 281–287. A modification of the Kjeldahl method, based on the use of a new mineralisation mixture, was used for the determination of N in isatin, benzotriazole, 1-phenylbenzotriazole, 2-phenylbenzotriazole and their derivatives. *Mineralisation mixture*—Mix 3 vol. of H_2SO_4 (96%) and 1 vol. of H_3PO_4 (65%) and divide into two portions. To the first add $CuSO_4.5H_2O$ (1 g per 100 ml), to the second add powdered selenium (1 g per 100 ml). Heat till dissolution is complete, cool, mix the two soln. and heat again. For 0·1 to 0·15 g of the sample use 15 to 22 ml of the mineralisation mixture. J. ZÝKA

3791. **Micro-determination of the sulphur content of organic compounds.** L. Mázor, T. Meisel and L. Erdey (Dept. Gen. Chem., Tech. Univ., Budapest). *Magyar Kém. Lapja*, 1959, **14** (12), 494–496.—Three published methods were studied and somewhat modified. In the method of Zinneke as modified by Večeřa (*cf. Anal. Abstr.*, 1955, **2**, 1238; 1958, **5**, 3365) the Grote tube was replaced by a more

easily assembled apparatus. The Ag^+ are determined with KI soln., either potentiometrically or by using Variamine blue (C.I. Azoic Diazo Component 35) as indicator. The results can be checked by titrating SO_4^{2-} in 80% ethanol with 0·005 *N* $Ba(ClO_4)_2$, with thoron as indicator (Mázor *et al.*, *Mikrochim. Acta*, 1960, 417). In the method of Schöniger (*Anal. Abstr.*, 1957, **4**, 924), the traces of air which remain in the flask form HNO_3 during combustion, so it is better to absorb in aq. H_2O_2, SO_4^{2-} then being titrated as already described. Zimmermann's method (*Mikrochemie*, 1943, **31**, 15) can be simplified by covering the sample in a test-tube with a 2 to 3-cm layer of small glass-beads. The potassium is placed on top and when it melts it runs down on to the sample. The absorbing vessel can be improved by coating it inside with a hydrophobic silicon compound. As an alternative, S^- can be determined after fusion of the sample with potassium by the method of Mázor *et al.* (*vide supra*).

A. G. Peto

3792. **Rapid determination of hydrolysable sulphur in organic compounds.** M. Wrónski (Dept. of Chem. Technol., Univ. of Łódź, Łódź, Poland). *Anal. Chem.*, 1960, **32** (1), 133–134.—Hydrolysable S, *i.e.*, that which forms sulphide after being boiled with *o*-hydroxymercuribenzoic acid (**I**) can be determined by back-titrating the excess of **I** with standard thioglycollic acid soln., with dithizone or thiofluorescein as indicator. To the sample (containing < 10 mg of hydrolysable S) dissolved in ethanol or water are added 5 ml of *N* NaOH and 20 ml (excess) of 0·03 *N* **I**. The mixture is boiled gently for 5 min. under reflux, with an additional 10 ml of ethanol if volatile compounds are present. The cooled soln. is made up to 100 ml, and excess of **I** is determined by one of the following methods. (*i*) Thiofluorescein soln. (0·02% in dil. aq. NH_3) (10 ml) is added and titration is carried out with thioglycollic acid soln. until a permanent blue colour appears. (*ii*) To the soln. are added 5 ml of sodium sulphide soln. and 0·5 ml of dithizone soln. and the mixture is titrated with a soln. of **I** until the colour changes from yellow to purple. The consumption of **I** for the sodium sulphide added is determined separately and subtracted from the result of the first titration. Reliable results can be obtained if the soln. is standardised under the conditions of the determination. The method may be applied to the rapid determination of wool.

S. M. Marsh

3793. **Micro-detection and micro-determination of some elements in organic compounds by means of decomposition with magnesium.** M. Jureček and J. Jeník (Inst. Chem. Technol., Pardubice, Czechoslovakia). *Sb. Věd. Prac., Vysoké Školy Chem.-Technol., Pardubice*, 1959, 105–112.—A survey of previously published work on the micro-detection of C, As and Hg in organic and inorganic compounds, and of iodine, P, As and Sb in organic compounds is presented. A new method for the detection of Hg is described. *Procedure*—Ignite the sample with metallic magnesium in a modified Zimmermann tube containing a crystal of iodine; the vapours of iodine and Hg react to form yellow HgI_2 which turns red. The method is suitable for detecting > 10 μg of Hg in ores or biological materials.

J. Zýka

3794. **Decomposition of organic substances with magnesium. VII. Micro-determination of iodine in organic compounds.** J. Jeník, V. Pátek and M. Jureček (Inst. Chem. Technol., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 4040–4042 (in German).—Decompose the sample by fusion with magnesium (Jureček and Jeník, *Anal. Abstr.*, 1957, **4**, 930), transfer the product to a 50-ml flask and dissolve it in acetic acid (30%) (8 ml). Add $Al_2(SO_4)_3$ soln. (2·5%) (5 ml) to coagulate colloidal C and set the mixture aside for 10 min. Filter through a sintered-glass filter, dissolve the residue in acetic acid by heating, and filter, washing the residue three times with $Al_2(SO_4)_3$ soln. Add cryst. Na acetate (4·5 g) and Br in glacial acetic acid (3 ml of Br in 17 ml of glacial acetic acid) (1 ml) to the filtrate, close the flask and mix the contents for 10 min. Add 7 drops of conc. formic acid and mix for 5 min. to remove Br, add 8 *N* H_2SO_4 (10 ml) and KI (0·2 g), close the flask and set it aside in the dark for 10 min., then titrate with 0·02 *N* $Na_2S_2O_3$, with starch as indicator. Carry out a blank.

J. Zýka

3795. **Chemical determination of amine functions. Application to long-chain aliphatic amines.** J. Mestreit. *Chim. Anal.*, 1960, **42** (1), 3–8.—Methods for determining primary, secondary and tertiary amines are reviewed and the application to long-chain amines of the reaction with CS_2 to form dithiocarbamic acids, followed by titration with KOH, is described. The amine index (defined as the no. of mg of KOH required to neutralise the dithiocarbamic acid formed from 1 g of amine) is determined for *n*-dodecylamine and found to be reliable only below 0°. Secondary and tertiary amines are determined in a mixture by formation of the Schiff base with 2-ethylhexaldehyde and primary amines before the treatment with CS_2. The determination of amines in water by the method of Milun and Moyer (*Anal. Abstr.*, 1956, **3**, 3480) is reviewed in detail.

E. J. H. Birch

3796. **Anomalous reactions in the determination of amino nitrogen. VII. The anomaly of the sulphonic acid amides.** G. Kainz and H. Huber (Chem. Inst., Univ. Wien, Austria). *Mikrochim. Acta*, 1960, (1), 38–43 (in German).—Unlike carboxylic acid amides, sulphonic acid amides readily evolve gas when treated with HNO_2. The gas usually contains ≃ 1·5 moles of N_2O and 0·25 mole of N unless iodide ion or iodine is added to the reaction mixture, when the gaseous product becomes a mixture of N_2O and N totalling ≃ 1 mole. It is suggested that the reaction takes place via the formation of the corresponding sulphinic acid with the liberation of 1 mole of N_2O plus N. This sulphinic acid reacts with HNO_2 to form a diaryl sulphonylhydroxylamine, which decomposes to form a sulphonic acid and 0·5 mole of N_2O. The addition of iodide ion or iodine oxidises the sulphinic acid to a sulphonic acid and prevents the formation of additional N_2O.

W. T. Carter

3797. **New microchemical reaction for nitroso compounds.** V. Anger (Lab. Dr. V. Anger, Wien, Austria). *Mikrochim. Acta*, 1960, (1), 58–61 (in German).—Nitroso compounds react with a 0·1% soln. of diphenylbenzidine in 85% H_2SO_4 to yield a blue quinonoidal dyestuff. The reaction has a sensitivity of ≃ 1 μg. Strong oxidising agents, such as nitrate, nitrite, chlorate, bromate and nitrate, and nitrite esters and certain quinones interfere, but hydroximino compounds do not.

W. T. Carter

3798. **Determination of reducing agents by means of the phosphomolybdenum blue procedure.** K. Schriever (Inst. f. Pharm. u. Lebensmittelchem., Univ., München). *Dtsch. ApothZtg*, 1960, **100** (2), 35.—*Procedure*—Dissolve the reducing agent (0·01 mole) in 40 ml of water containing 3 g of $Na_2S_2O_5$ and 2 g of $Na_2SO_3.7H_2O$. Mix 1 ml of a soln. containing 0·4393 g of KH_2PO_4 per litre with 3 ml of a soln. containing 4 g of $Na_2MoO_4.2H_2O$ in 100 ml of 5 *N* H_2SO_4 and dilute with 10 ml of water. Warm to 37°, add 1 ml of the reducing agent soln., maintain at 37° for exactly 2 min., read the extinction of the blue soln. and refer the results to a standard curve. Strong reducing agents, *e.g.*, 1:4-dihydroxynaphthalene, are suitably determined by means of a molybdoarsenic acid reagent.

A. G. COOPER

3799. **Paper chromatography of olefins.** W. Huber (Badische Anilin- & Soda-Fabrik A.-G., Ludwigshafen am Rhein, Germany). *Mikrochim. Acta*, 1960, (1), 44–53 (in German).—Olefin - mercury adducts are prepared by treating olefins with excess of mercuric acetate in methanol at room temperature; they are separated by paper chromatography with a mobile phase containing aq. NH_3, ammonium carbonate soln. and either *n*-propanol, *n*-butanol or *iso*amyl alcohol. The separated compounds are located by treating the paper with HCl vapour and spraying with $(NH_4)_2S$ or dithizone soln. Quantitative results with a precision of ±7·5% can be obtained by direct photometry after impregnating the paper with liquid paraffin and bromonaphthalene, or the spots can be eluted and their mercury content determined colorimetrically with dithizone. R_F values increase with increasing molecular weight, and isomers are separable for the C_3 to C_6 olefins. Diolefins have very low R_F values and should be separated by distillation before chromatography to avoid confusion with low-molecular-weight mono-olefins. W. T. CARTER

3800. **Infra-red and Raman spectra of the pentafluoroethyl halides.** O. Risgin and R. C. Taylor Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Spectrochim. Acta*, 1959, **15** (12), 1036–1050.—Pentafluoroethyl halides have been investigated in the gaseous and liquid state. Results of measurements of the Raman and i.r. spectra are tabulated, giving frequency, assignments and symmetry. The increasing intensities of certain groups of frequencies in the Raman spectra due to increasing polarisability, and frequency shifts due to increasing mass, in the Cl - Br - I series are used to assign fundamental modes, 18 of which have been identified and assigned. These assignments are compared with those of Nielsen *et al.* (*J. Chem. Phys.*, 1953, **21**, 383), Klaboe and Nielsen (*Ibid.*, 1959, **30**, 1375) and Barcelo (*J. Res. Nat. Bur. Stand.*, 1950, **44**, 521). Evidence for the correctness of the present assignments is given as a correlation diagram for the fundamental frequencies of the pentafluoro compounds and ethyl hexafluoride. Assuming rigid rotation about the C–C axis, barrier heights of the potential hindering internal rotation are also calculated from the torsional oscillation frequency observations. An empirical correlation is also given between the observed barrier heights and the over-lap of the two interacting terminal halogen atoms. G. P. MITCHELL

3801. **Chromatographic separation of microgram amounts of butyl and *iso*octyl alcohols.** T. G. Lipina. *Zavod. Lab.*, 1960, **26** (1), 55–57.—The sample is dissolved in 2 ml of benzene and treated with 0·2 ml of a soln. of 50 mg of 3:5-dinitrobenzoyl chloride in 30 ml of benzene and one drop of a 10% soln. of pyridine in benzene and the benzene is evaporated off. The 3:5-dinitrobenzoates are then separated chromatographically on silica gel treated with Rhodamine 6G (C.I. Basic Red 1) and made into a paste with starch, which is spread on a glass plate 15 mm × 220 mm. Light petroleum (boiling-range 85° to 110°) is used as solvent, and the zones are separated by means of a 10% soln. of diethyl ether in light petroleum, filtered u.v. radiation (320 to 380 mμ) being used for locating them. The separated compounds are dissolved in diethyl ether (3 ml) and determined photometrically at 575 mμ as the coloured complexes that are formed by reaction with acetone and NaOH. The method is applicable to the separation of between 10 and 200 μg of the dinitrobenzoates and it is sensitive to 5 μg. G. S. SMITH

3802. **Glycerine (glycerol).** British Standards Institution (2 Park St., London, W.1). B.S. 2621–5: 1955. Amendment No. 1 (4.4.60).—The method for the determination of glycerol content is changed.

3803. **Indirect method of determining optical rotation of some monosaccharides.** C. C. Spencer and C. J. McGinn (Syracuse Univ., Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 136.—When a 40:1 excess of a monosaccharide is allowed to react with aq. periodic acid, the next lower monosaccharide is produced. The specific rotation of the reaction product can be calculated without its isolation by subtracting the contribution to the observed rotation made by the excess of the original monosaccharide. A. R. ROGERS

3804. **Acetic acid.** British Standards Institution (2 Park St., London, W.1). B.S. 576:1950. Amendment No. 2 (10.3.60).—The specification is extended to cover glacial acetic acid for photographic use.

3805. **Volumetric estimation of formates by oxidation with mercuric chloride.** R. M. Verma and S. Bose (Dept. of Chem., Mahakoshal Mahavidyalay, Jabalpur, India). *J. Indian Chem. Soc.*, 1960, **37** (1), 47–49.—A neutral soln. of formate (10 to 20 ml) containing 10 to 100 mg of formic acid is treated with 30% Na acetate soln. (5 ml) and saturated $HgCl_2$ soln. (25 ml). The mixture is immersed in boiling water for 40 min. and then acidified with conc. HCl (50 ml), and cooled. The final acidity of the soln. should be at least 4 *N*. About 5 ml of CCl_4 is added to the flask and the contents are titrated with 0·1 *N* KIO_3 until the aq. layer becomes pale yellow. The titration is continued by adding small portions of iodate soln. followed by vigorous shaking of the flask until the last trace of violet coloration disappears from the organic layer. The error of the method is about +0·5%. Many carboxylic acids do not interfere, *e.g.*, lactic, butyric, acetic, propionic, tartaric, citric and benzoic acids. The method cannot be used in the presence of aldehydes or salts of salicylic, adipic, malonic, phthalic, oxalic, aminoacetic, phenylacetic, fumaric and maleic acids. G. S. ROBERTS

3806. **Paper-chromatographic separation and identification of the C_1 to C_6 fatty acids as the 2:4-dinitrobenzyl esters.** M. Jureček, J. Churaček and V. Červinka (Inst. Anal. Chem., Chem.-Technol. Inst., Pardubice, Czechoslovakia). *Mikrochim.*

Acta, 1960, (1), 102–112 (in German).—The 2:4-dinitrobenzyl esters are prepared by heating the mixture of the sodium salts of the acids with the theoretical amount of 2:4-dinitrobenzyl bromide in a sealed ampoule in a water bath for 1 hr. The esters are then separated by ascending chromatography on paper impregnated with 25% ethanolic formamide soln., with *cyclo*hexane - benzene (21:1) as mobile phase. The separated spots are located by spraying with a mixture of satd. ethanolic Na ethoxide soln. and acetone (1:3). The formic acid ester, if present, remains at the origin and is separated on a second chromatogram by using paper impregnated with a petroleum fraction and 65% ethanol as the mobile phase. Isomers are not separable. The presence of free 2:4-dinitrobenzyl bromide on the chromatogram must be avoided since it masks the spot due to the propionic acid ester. The limit of detection for acetic acid is $\simeq 1$ μg. W. T. CARTER

3807. **Use of bromine chloride as volumetric reagent. New procedure for the determination of maleic and fumaric acids.** K. Burger and E. Schulek (Inst. for Inorg. and Anal. Chem., Eötvös Univ., Budapest, Hungary). *Z. anal. Chem.*, 1960, **172** (2), 98–105 (in German).—An excess of BrCl reagent (prep. described) is added to the sample and acidified with HCl. When the reaction is completed (2 hr. for maleic acid and 6 hr. for fumaric acid, respectively), the excess of BrCl is back-titrated iodimetrically. The error of the method is ± 1·5%. Maleic acid (2 to 5 mg) in the presence of > 6 mg of fumaric acid in a total vol. of 15 ml is neutralised to methyl red, 5 drops of $HgSO_4$ soln. (0·5 *M*) are added, with stirring, and after 1 hr. the mixture is centrifuged. The supernantant liquid is filtered, an excess of 0·01 *M* BrCl is added and maleic acid is determined as before. The method has been applied to polyester resins. B. B. BAUMINGER

3808. **Infra-red spectra of crystalline adipic acid and deuterated analogues.** H. Susi (E. Region Res. Lab., Philadelphia, Pa., U.S.A.). *Spectrochim. Acta*, 1959, **15** (12), 1063–1071.—A study of the i.r. spectra of crystalline adipic acid and its partially and fully deuterated analogues in the 400 to 4000-cm^{-1} region is reported. Wavelengths, approx. intensities, polarisations and assignments are tabulated. From structural considerations in adipic acid, 21 i.r.-active fundamental modes are possible, 19 of which have been assigned on the basis of deuteration shifts and polarisation measurements. By analogy between adipic acid and higher analogues in the region 1180 to 1360 cm^{-1} (Corish and Davidson, *J. Chem. Soc.*, 1957, 1746), the increasing number of bands can be regarded as arising from mixed molecular B_u fundamentals involving carboxyl deformation, CH_2 wagging and CC stretching. G. P. MITCHELL

3809. **Photometric indicator titration of weak bases in acetic acid. The modified type-II plot.** K. A. Connors and Takeru Higuchi (Sch. of Pharm., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 93–96.—The procedure described takes into account solvolysis of the salt formed during titration. Exchange constants and quant. recovery data are reported for the titration of acetamide, urea, 2:6-dimethyl-4*H*-pyran-4-one, thiourea, caffeine, phenazone and triphenylguanidine in acetic acid with various indicators. Recoveries of 98 to 101% were obtained for all samples in the 20 to 30-mg range. K. A. PROCTOR

3810. **Micro-titrations of organic bases in non-aqueous solvents.** M. Gutterson and T. S. Ma (Dept. of Chem., Brooklyn Coll. of New York City, U.S.A.). *Mikrochim. Acta*, 1960, (1), 1–11 (in English).—Satisfactory titrations can be carried out with 0·01 *N* $HClO_4$ in dioxan with acetic acid or acetic anhydride as solvent. The end-point may be detected potentiometrically with a pH meter or a visual indicator may be used, the most suitable being crystal violet, triphenylmethanol, neutral red and dibenzylideneacetone. Acetic anhydride is suitable for the titration of bases with pK_b values (in water) of up to 13·5, while for acetic acid the upper limit is $\simeq$ 12·0. Water interferes and the solvent used should contain < 1%. The results obtained by both methods of end-point detection agree to within 2%, but the results for titrations with indicators are more precise. Potentiometric titrations were also carried out in formic acid and propionic acid as solvents, but the usefulness of formic acid was limited by its instability and of propionic acid by the high water content of the commercially available material. W. T. CARTER

3811. **Chromatography of organic compounds. IV. Determination of ethanolamines with paper chromatography.** J. Franc and M. Hájková (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 4043–4045 (in Russian).—The mixture of mono-, di- and tri-ethanolamines is separated chromatographically on Whatman No. 1 paper by the descending technique and with dimethylformamide - ethanol (3:7) as solvent. The separated compounds can be detected with catechol violet soln. (0·2 to 0·3%) or a mixture of Gibbs's reagent (0·5 g of 2:6-dibromo-*p*-benzoquinone-4-chlorimine and 0·3 g of phenol dissolved in 100 ml of ethanol) with *m*-cresol. The separated spots can be cut out, eluted by immersion for 12 hr. in H_2O and titrated with 0·05 *N* HCl, with 2:6-dichlorophenolindophenol soln. as indicator. J. ZÝKA

3812. **Identification of fragments in the mass spectra of dialkyldiboranes.** C. O. Wilson, jun., and I. Shapiro (Res. Lab., Olin Mathieson Chem. Corp., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 78–81.—The mass spectra of 1:1- and 1:2-dimethyldiboranes and their ethyl analogues have been analysed. The identification of fragments is aided by using isotopically labelled compounds. Some alkyl rearrangement with 1:2-dialkyldiboranes has been noted. K. A. PROCTOR

3813. **Gas - liquid partition chromatography of *m*- and *p*-xylenes on 1-naphthylamine.** Takeo Araki and Ryozo Goto (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Bull. Chem. Soc. Japan*, 1960, **33** (1), 115 (in English).—The separation of *m*- and *p*-xylenes, with 1-naphthylamine as the stationary liquid phase on C-22 firebrick, is described. Because of the instability of 1-naphthylamine, the end of the column (approx. 7 cm) is packed with bare solid support to maintain a stable base line. When ethylbenzene is present in the samples, it is not separated from *p*-xylene. I. JONES

3814. **Analyses of o-xylene oxidation products.** H. E. Lumpkin and D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 74–77.—Distillation and chromatographic fractions from the products obtained by catalytic oxidation of *o*-xylene have been examined by infra-red and mass spectrometry.

Results are given and discussed. *o*-Xylyl *o*-toluate and C_{15} and C_{16} diaryl hydrocarbons are shown to be present, and phthalide is a major oxidation product. S. M. MARSH

3815. **Analysis by means of gas - liquid chromatography of products of manufacture of phenol and synthetic ethanol.** A. N. Korol'. *Zavod. Lab.*, 1960, **26** (1), 51–54.—The use of gas chromatography for analysing mixtures containing benzene, ethylbenzene, *iso*propylbenzene and polyalkylbenzenes and others containing diethyl ether, acetic anhydride and *iso*propyl alcohol is described. G. S. SMITH

3816. **Separation of the C_7 to C_{14} alkylphenols with paper chromatography.** J. Macák and J. Kubeš (Dept. for Gas and Coke Production, Inst. Chem. Technol., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 301–303 (in German).—The developing solvent used is *cyclo*hexane with Whatman No. 1 or 4 paper or the German WF-1 (DDR) impregnated with either ethanolic formamide soln. (20%), ethanolic acetamide soln. (20%) or aq. NaOH soln. (4%), the first being preferred in most cases. A benzene soln. of about 0·08 mg of the substance was applied to the paper. Either the descending or the ascending technique was applicable. R_F values are given for 18 alkylphenols. J. ZÝKA

3817. **Analysis of solutions of alkali phenoxides.** S. K. Chirkov (A. M. Gorki Ural State Univ.). *Zavod. Lab.*, 1959, **25** (10), 1177–1180.—Electrometric non-compensated titration with a tungsten-wire indicator electrode and a copper - copper sulphate reference electrode is carried out with *N* H_2SO_4 for the determination of NaOH, Na_2CO_3 and Na phenoxide. G. S. SMITH

3818. **The carbonyl stretching frequency of *cyclo*pentanone.** C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Noack, R. J. D. Smith and R. N. Jones (Nat. Res. Council of Canada, Ottawa). *Spectrochim. Acta*, 1959, (11), 926–931.—Examination of the infra-red and Raman spectra of $\alpha\alpha'\alpha'$-tetradeutero*cyclo*pentanone has led to a Fermi resonance interpretation of the splitting of the carbonyl stretching band in *cyclo*pentanone. E. G. CUMMINS

3819. **Determination of *p*-toluic and terephthalic acids in the presence of each other.** V. Kudláček, J. Bořek and P. Kratochvíl (Dept. Org. Chem., Inst. Chem. Technology, Pardubice, Czechoslovakia). *Sb. Věd. Prac., Vysoké Školy Chem.-Technol., Pardubice*, 1959, 289–298.—Visual, gravimetric and potentiometric titrations in non-aqueous medium were examined for use in the analysis of the products obtained by the oxidation of *p*-dialkylbenzenes with HNO_3 under pressure. The most rapid and accurate procedure was found to be a back-titration method after previous pptn. of the sample as the sodium salts. J. ZÝKA

3820. **Determination of organic nitro, nitroso and azo compounds with copper.** R. S. Juvet, jun., M. C. Twickler and L. C. Afremow (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (1), 87–92 (in English).—*Procedure*—Mix 20 ml of ethanol or di-(2-methoxyethyl) ether (distilled over copper) with 20 ml of 6 *N* H_2SO_4, de-aerate the mixture by adding solid carbon dioxide, and add sufficient of the nitro, nitroso or azo compound to oxidise 0·5 to 1 g of Cu. Add 6 to 15 g. accurately weighed, of cleaned copper foil, 0·002 in. thick, in pieces 1 cm square and bent into cylinders. Boil under a reflux condenser for 1 to 2·5 hr. while passing a stream of CO_2. Cool, decant the liquid, wash the remaining copper with de-aerated water and de-aerated acetone, dry it *in vacuo* and determine its loss in wt. Correct for a blank value determined on the reagents. Each nitro group oxidises 6 equiv. of Cu. The accuracy is $\pm 0{\cdot}5\%$. The method fails with 1-nitronaphthalene, 2-methyl-1-nitronaphthalene, 2:4-dinitrophenylhydrazine and *m*-iodonitrobenzene. Aliphatic nitro compounds are reduced quant. only after prolonged boiling. H. N. S.

3821. **Cathodic action of the phenylenediamine dihydrochlorides at the dropping-mercury electrode.** S. R. Cooper and O. F. Fowlkes (Howard Univ., Washington, D.C., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 26–27.—The method described can be used to determine the three isomers which, when dissolved in tetramethylammonium bromide, with gelatin as a max. suppressor, give well-defined waves in the 10^{-3} *M* range. A plot of i_d against concn. gives reasonably straight lines with the *ortho* and *para* compounds and not much deviation from linearity with the *meta* isomer. K. A. PROCTOR

3822. **Photometric determination of benzidine, diphenyline, o-benzidine, o-tolidine and o-dianisidine.** V. Kratochvíl, M. Matrka and J. Marhold (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 101–107.—The method is based on the tetrazotisation of the sample and coupling of the tetrazonium salt formed with N-ethyl-1-naphthylamine (**I**). *Procedure*—To 5 ml of the soln. of the sample (containing 0·01 to 0·1 mg of the substance) in 0·1 *N* HCl add *N* HCl (4 ml for diphenyline and *o*-benzidine, 2 ml for benzidine and *o*-tolidine, 1 ml for *o*-dianisidine). Cool to 0° to 5°, add $NaNO_2$ soln. (1%) (1 ml) and mix; after 5 to 10 min. remove from the ice bath, add sulphamic acid soln. (5%) (1 ml), mix for about 2 min., add **I** soln. (0·2% in 96% ethanol) (1 ml), dilute to 50 ml with ethanol, mix and measure the extinction at 620 mμ for benzidines or 545 mμ for diphenyline. Compare with a calibration curve. J. ZÝKA

3823. **Colorimetric determination of 3:5-dinitro-o-toluamide and related dinitro compounds.** G. N. Smith (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 32–37.—The method is based on the reaction of the 3:5-dinitro-*o*-toluamide (**I**) with dimethylformamide and methylamine to give a purple complex, which is then examined spectrophotometrically. An acetone soln. of an unknown sample of **I** (1 ml) (containing 500 μg of **I**) is mixed with 24 ml of dimethylformamide, previously cooled to 20°; 25 ml of 40% methylamine soln. at 3° to 5° is then added. After exactly 3 min. the colour of the soln. is compared spectrophotometrically, at 390 and 550 mμ, with that obtained simultaneously from an aliquot of standard **I** soln. The effects on colour formation of methylamine concn., temp., organic solvents, aliphatic amines and other chemicals, and the stability of the complex are discussed. The reproducibility of the method is $\pm 1\%$. Results of a study of the specificity of the reaction are tabulated and spectral curves are presented. By examination of the

secondary absorption peaks it is possible to determine the amount of each isomer in a mixture of dinitrotoluamides to within ±2%.

S. M. MARSH

3824. **Determination of isomers in technical tritolyl phosphate by means of partition chromatography.** M. N. Obotova. *Zavod. Lab.*, 1959, **25** (10), 1184–1186.—A method based on that of Franc (*Coll. Czech. Chem. Commun.*, 1955, **20**, 298) is described. The reagent used for the photometric determination of cresols in the eluate is diazotised *p*-nitroaniline. G. S. SMITH

3825. **Amperometric titration of mercaptobenzothiazole solution.** Yu. I. Usatenko and G. E. Bekleshova. *Ukr. Khim. Zhur.*, 1959, **25** (4), 512–515; *Ref. Zhur., Khim.*, 1960, (6), Abstr. No. 22,070.—It is shown that 2-mercaptobenzothiazole (**I**) is oxidised on a rotating platinum anode giving a wave at + 0·4 V *vs.* the S.C.E., the height of which is proportional to the concn. of **I** in the soln. Amperometric titrations are described for Ag^+ and for Cu^{2+} which form sparingly sol. compounds with **I**. Titrate with a 0·05 to 0·005 *M* soln. of **I** in 0·1 *M* KOH, with an e.m.f. of + 0·5 V for the oxidation of **I**. To titrate Ag (0·05 to 10 mg) use a 0·1 *M* aq. NH_3 basal soln. in an acetate - succinate - borate buffer soln. (pH 3 to 7). The ppt. has the composition Ag: **I** = 1:1; NH_4^+, Cl^-, Ni^{2+} and Zn^{2+} (when NH_4^+ are present), and Cu^{2+} in an amount equal to the Ag^+ content, do not interfere. In the presence of large amounts of Cu^{2+}, separate silver as AgCl, dissolve the ppt in aq. NH_3 soln., neutralise with HCl soln., add 2 *M* aq. NH_3 (5 ml) and titrate with **I** soln. Titrate Cu^{2+} (0·05 to 0·005 *M*) with a 0·1 *M* basal soln. of KNO_3, NaCl, K_2SO_4, NH_4Cl, $(NH_4)_2SO_4$, or aq. NH_3 - NH_4Cl soln. at 20° or preferably at 60°. Both amperometric titrations and chemical methods show that, in the absence of NH_4^+, the composition of the ppt. is in the ratio of Cu: **I** = 1:1, whereas, in the presence of NH_4^+ it is in the ratio of 1:2.

K. R. C.

3826. **The infra-red spectrum and structure of crystalline ferrocene.** W. K. Winter, B. Curnutte, jun., and S. E. Whitcomb (Dept. of Physics, Kansas State Univ., Manhattan, U.S.A.). *Spectrochim. Acta*, 1959, **15** (12), 1085–1102.—Theoretical aspects of the ferrocene molecular and crystal structure are discussed with respect to point group, site group and factor group symmetry considerations. The growth and orientation of single crystals of ferrocene are described, together with practical details for recording the i.r. spectra of a single crystal in the region 450 to 6000 cm^{-1}, with a Perkin - Elmer 12-C spectrometer and plane-polarised exciting radiation. The observed i.r. frequencies, together with tentative assignments and species, are tabulated and support the assignments of Lippencott and Nelson (*Spectrochim. Acta*, 1958, **10**, 307). The polarisation data indicate that the molecular symmetry axis lies nearly in the t_1t_2 plane of the unit cell and the angle between it and the t_2 axis is approx. $\pi/4$.

G. P. MITCHELL

3827. **Paper chromatography of naphtholsulphonic acids.** J. Kolšek and M. Perpar (Inst. for Org. Chem., Univ., Ljubljana, Yugoslavia). *Chemiker Ztg*, 1959, **83** (21), 712–714.—Twenty-three commercial samples of fifteen different naphtholsulphonic acids have been examined by paper chromatography with the solvent *tert.*-butyl alcohol - *n*-butanol - water (4:3:3). R_F values are given for the major components and impurities. The max. extinction of the chromatographically pure substances are also listed. N. E.

3828. **Specific thermochromic detection of anthracene compounds.** T. R. Hauser (Taft San. Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Chemist Analyst*, 1959, **48** (4), 86–87.—Anthracene and its simple deriv. can be oxidised with a saturated soln. of CrO_3 in acetic acid to the corresponding 9:10-anthraquinones. The deriv. is recovered by extracting the reaction mixture with $CHCl_3$ and evaporating to dryness. A minimum quantity of dimethylformamide is used to dissolve the residue and the soln. is then boiled with potassium borohydride. The test is positive if the soln. changes colour reversibly from colourless at room temp. to red at the boiling-point. Inner-ring polycyclic *p*-quinones and fluorenones also give a positive test and must be proved absent by dissolving a portion of the sample in dimethylformamide and boiling with potassium borohydride. An identification limit of $\simeq 15\ \mu g$ is claimed. Large amounts of several related polynuclear hydrocarbons give a positive test.

G. S. ROBERTS

3829. **Colorimetry of furfuraldehyde. II. Reaction with phenols of the resorcinol type.** F. Aeschlimann, P. O. Bethge and J. H. Eggers (Swedish Inst. f. Wood Res., Stockholm). *Z. anal. Chem.*, 1960, **172** (4), 241–256 (in German).—The colour reaction of furfuraldehyde (**I**) with *m*-dihydroxybenzene analogues (**II**) by which **I** is detected and determined in Tollens distillates in the presence of 5-methylfurfuraldehyde and 5-hydroxymethylfurfuraldehyde (**III**) is studied. A comparison of several phenols shows that under standardised conditions *m*-cresol, 3:5-xylenol, and 2:3:5-trimethylphenol behave analogously to **II**, *i.e.*, a methyl group can replace a hydroxyl group in the reagent. The reaction products are complex mixtures. Under mild conditions, only **II** react and in a reducing medium differences in colour between the products from **I** and **III** may be suppressed. For the quant. determination of **I** (optimum concn. 0·02%) in Tollens distillates, 5-methylresorcinol is the only suitable reagent, in spite of deviations from Beer's law, as the others produce excessive spectral overlap between the products from **I** and **III**. The deviations from Beer's law depend on the concn. of Fe^{3+} and Cu^{2+} present, but the curves are reproducible.

J. P. STERN

3830. **Modified Ehrlich benzaldehyde reagent for the detection of indoles on paper chromatograms.** H. Sprince (Lab. of Res. Biochem., U.S. Veterans Admin. Hosp., Coatesville, Pa.). *J. Chromatography*, 1960, **3** (1), 97–98.—An increased rate of response and an improved colour stability are obtained by spraying with 2% *p*-dimethylaminobenzaldehyde soln. in conc. HCl followed 2 to 3 min. later by 1% $NaNO_2$ soln. W. T. CARTER

3831. **Paper-chromatographic separation of phenazine derivatives.** L. Birkofer and G. Leithäuser-Weitecki (Chem. Inst., Univ., Köln, Germany). *Naturwissenschaften*, 1959, **46** (24), 669.—Phenazine derivatives can be separated by ascending reversed-phase paper chromatography with a hydrophobic (2043a "hy" S. & S.) or acetylated (2043b acetylated S. & S.) paper, with either

an acid solvent system (butanol - acetic acid - water, 4:1:5, or butanol - acetone - acetic acid - water, 3:1:1:5) or an alkaline system (conc. aq. NH_3 saturated with butanol). Separation is better with an alkaline medium except that some derivatives with a quaternary nitrogen atom are oxidised by atmospheric oxygen. Results for 16 typical compounds with both types of paper and solvent system are tabulated. The position of the compounds on the chromatogram is determined by viewing in ultra-violet light, when the flecks have either a yellow or red fluorescence or appear as dark spots. S. M. MARSH

3832. **Ultra-violet absorption spectra of derivatives of symmetric triazine. III. The guanylmelamines [amidinomelamines].** R. C. Hirt, F. Halverson and F. T. King (Central Res. Div., American Cyanamid Co., Stamford, Conn., U.S.A.). *Spectrochim. Acta*, 1959, (11), 962–968.—The determination of the u.v. absorption spectra of mono-, di- and tri-amidinomelamine, phenylamidinomelamine and phenylguanidine, and their ions, and the spectroscopic measurement of their ionisation constants are reported. The conjugation of the guanidino-group C:N double bond with the triazine ring, proposed for the un-ionised forms, is lost in the ionic form. E. G. CUMMINS

3833. **1-Phenyl-3-pyrazolidone (photographic grade).** British Standards Institution (2 Park St., London, W.1). B.S. 3230 : 1960. 8 pp.—Methods are given for the determination of melting-point, ash, iron, heavy metals and reducing agents.

3834. **Ultra-violet spectrophotometric determination of 1:10-phenanthroline.** P. J. Secrest, J. A. Pawley and C. A. Lucchesi (Anal. Res. Dept., Sherwin-Williams Co., Chicago, Ill., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (6), 141–143.—A rapid method is described for the determination of 1:10-phenanthroline in its technical grade, which is used as a drying catalyst in oils, varnishes and paints. The difference in extinction of an ethanolic soln. of the sample at 323·5 and 320 mμ is an approx. measure of the 1:10-phenanthroline content. A more exact determination may be made by a differential comparison of the base-line extinction at 323·5 mμ of the sample soln. with that of a reference soln. The standard deviation of the method is $< \pm 0{\cdot}2\%$, and good agreements were obtained with results of a colorimetric method based on formation of a red complex with Fe^{2+}. P. T. BEALE

3835. **Gas chromatography applied to continuous control of industrial plants. I. Analysis of a mixture of C_1 to C_4 hydrocarbons.** A. Rio, D. Ripa and S. Tribastone (Soc. Cementisegni, A.B.C.D.-S.A.M.A., Colleferro, Italy). *Chim. e Ind.*, 1959, **41** (12), 1185–1188.—A method for the determination of C_1 to C_4 hydrocarbons, as applied to the continuous control of an olefin steam-cracking unit, is described. The use of various stationary phases [di-(2-ethylhexyl) sebacate, tetra*iso*butylene and di-*iso*decyl phthalate] is described, and many standard retention times are tabulated. C. A. FINCH

3836. **Determination of di*cyclo*pentadiene by the Ritter - Gude method.** S. Higuchi (Tokyo Gas Co., Yokohama, Japan). *BrennstChemie*, 1960, **41** (1), 20–25.—The method (*cf. Anal. Abstr.*, 1958, **5**, 2265) is satisfactory provided that the phenyl azide used is purified by washing with water, and that complete reaction in samples containing $< 10\%$ of di*cyclo*pentadiene is ensured by allowing more time and using a higher proportion of azide. *cyclo*Pentadiene, which easily dimerises, should be distilled from the sample at 60° to 70° under reduced pressure. No interference is caused by CS_2, thiophen, *cyclo*hexene or di*iso*butylene, but indene and di-*cyclo*pentadiene oxide cause small errors. A. R. PEARSON

3837. **Testing liquid fuels. Rapid determination of tetraethyl-lead in petrol by decomposition with hydrochloric acid and complexometry. DIN 51781.** Fachausschuss Mineralöl- und Brennstoffnormung (Hamburg 1, Klosterwall 4, IV, City-Hof, Block B). *Erdöl u. Kohle*, 1959, **12** (12), 987–989.—This is a tentative standard published in Dec., 1959. The method is not applicable to samples containing multivalent metals. The sample is boiled with HCl to decompose the tetraethyl-lead, diluted with H_2O, neutralised, and buffered to a pH value between 10 and 11. A known excess of EDTA soln. is added and the excess is back-titrated with $ZnSO_4$ soln. G. BURGER

3838. **Detection and determination of manganese in petrol.** M. Pedinelli (Soc. Lavorazioni Org. Inorg., Trento, Italy). *Chim. e Ind.*, 1959, **41** (12), 1180–1184.—Methods for determining Mn in recently developed anti-knock compounds (*cyclo*pentadienylmanganese tricarbonyl and methyl-*cyclo*pentadienylmanganese tricarbonyl) are described. The petrol (50 ml) is extracted first with bromine (3 to 8 ml), then with H_2SO_4 - HNO_3 - H_2O (1:1:2 ml), and the extracted Mn is oxidised with KIO_4 (0·4 g). The resulting permanganate is determined spectrophotometrically at 520 mμ. A suitable calibration curve is given. A determination in the range of 0·03 to 0·3 g of Mn per U.S. gallon has an average deviation of 0·002 to 0·004 g per gallon, and takes about 2 hr. C. A. FINCH

3839. **Determination of porphyrins in crude petroleum.** J. Sanik, jun. [Res. and Develop. Dept., Standard Oil Company (Indiana), Whiting, U.S.A.]. *Anal. Chim. Acta*, 1959, **21** (6), 572–578 (in English).—Metal - porphyrin complexes are broken down by stirring a soln. of the sample in benzene with acetic acid satd. with HBr for 6 hr. at 45°. The aqueous phase is filtered through a cotton filter and a Celite column. The oil phase is shaken with 20% HCl and the aqueous phase is filtered through the cotton filter and Celite column. The filter and column are washed free from porphyrins with 20% HCl, and the filtrates and washings are combined and extracted with $CHCl_3$. The $CHCl_3$ extract is washed free from HCl by treatment with water, and the porphyrin content is determined by spectrophotometry at 500 mμ against $CHCl_3$. The effects of the several variables in the method have been evaluated and the results obtained on a specimen petroleum are in good agreement with those obtained by other methods. T. R. ANDREW

3840. **Determination of low sulphur concentrations in oils and organic solids.** E. W. Seefield and J. W. Robinson (Esso Res. Lab., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (1), 61–65 (in English).—A method is presented for the determination of S in organic solids, waxes and gas oils in the range 10 to 300 p.p.m. The sample is burned in a current of oxygen in a unit that consists of two

furnaces. In the first the initial combustion takes place at a temp. of 950° F, and the gaseous products pass on through the second furnace which is maintained at 2500° F. Combustion is completed by moving the boat on to the second furnace. The products contain the S as an equilibrium mixture of SO_2 and SO_3. The SO_3 is absorbed in an aq. soln. of $HgCl_2$ and NaCl with the formation of disulphitomercuric ions. The subsequent addition of a soln. of pararosaniline bleached with HCl, and formaldehyde soln., produces a red - violet colour, and the extinction at 560 mμ is a measure of the SO_2 present. The method is calibrated by burning a pure compound of S. Nitrogen (> 100 mg), Cl^- and organic compounds containing Cl interfere.

H. N. S.

3841. **Spectrofluorimetry of lubricating oils: determination of oil mist in air.** C. A. Parker and W. J. Barnes (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Analyst*, 1960, **85**, 3–7.—A recording spectrofluorimeter was used for investigating the fluorescence emission and excitation spectra of a variety of lubricating oils, particularly those used in compressors. The oils used showed a fluorescence emission band in the region of 2·8 μ^{-1} (357 mμ). Typical spectra obtained with light of frequency 4·03 μ^{-1} (248 mμ) are shown. The spectra are all similar, although the shape and precise position of the maximum varies from one sample to the next. An apparatus is described for sampling the air through a filter-paper. The fluorescence emission and excitation spectra of the eluate with *cyclo*hexane of the stained portion of the paper are measured and compared with those obtained by using a known concn. of the sample of oil taken from the sump of the compressor immediately after taking the sample of air. A blank determination is made on the unexposed part of the paper. Less than 1 μg of oil per litre of air can be determined.

A. O. Jones

3842. **Methods for the analysis and testing of coal and coke. Part 15. Fusibility of coal ash and coke ash.** British Standards Institution (2 Park St., London, W.1). B.S. 1016 : Part 15 : 1960. 13 pp.—Methods are given for preparation of the ash and the determination of fusibility temp.

3843. **Test methods for bitumen.** British Standards Institution (2 Park St., London, W.1). B.S. 3235 : 1960. 44 pp.—Tests are described for ash, ductility, flash-point and fire-point, loss on heating, penetration, softening-point, solubility in CS_2, and water content.

3844. **Quantitative determination of water in samples containing substances that react with the Karl Fischer reagent.** Jun Matsudaira and Kaname Muroi (Res. Lab., Mitsubishi Kasei Chem. Co., Hisamoto-cho, Kawasaki). *Japan Analyst*, 1959, **8** (7), 429–432.—Co-distillation of water with toluene (**I**) was examined for the determination of water content in offset printing ink, soap, caustic soda and fluorescent paint. For < 50, and 50 to 100 mg of water, 40 and 100 ml of **I** are necessary, the distillation being completed within 15 and 30 min., respectively. The end-point of the subsequent titration is not sharp in the presence of > 150 ml of **I** in 50 ml of methanol. Similar results were obtained with xylene.

K. Saito

3845. **Use of cellulosic ion exchangers for determination of quaternary ammonium compounds.** L. D. Metcalfe (Res. Div., Armour and Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 70–72.—Long-chain quaternary ammonium compounds may be determined by placing a soln., or a $CHCl_3$ extract from solid samples (*e.g.*, animal feeding-stuffs), on a column packed with partially carboxymethylated cellulose. The column is then given a preliminary washing with 25 ml of ethanol followed by 25 ml of water; *N* ethanolic HCl (5 ml) is added and the column is washed with 30 ml of water. The washings are placed in a separating-funnel and mixed with 250 ml of $CHCl_3$ and 1 ml of bromophenol blue indicator for 1 min. The $CHCl_3$ layer is transferred to a second funnel containing 1% Na_2CO_3 soln. and shaken for 15 sec. If quaternary ammonium compounds are present the $CHCl_3$ layer is blue. This is then transferred to a stoppered flask and dried over 0·5 g of anhyd. Na_2SO_4 for 30 min. The extinction of the soln. is measured at 603 mμ, with $CHCl_3$ as a blank. The column is regenerated by washing with water until the washings are no longer acid and then washing with 10 ml of ethanol. Care must be taken to clean soap and anionic detergents from any glass-ware used since these react to give low results. Typical results are tabulated.

S. M. Marsh

3846. **Determination of citral in lemongrass oil and citrus oils by condensation with barbituric acid.** L. Levi and P. M. Laughton (Food and Drug Lab., Dept. of Nat. Hlth and Welfare, Ottawa, Canada). *J. Agric. Food Chem.*, 1959, **7** (12), 850–859.—A highly specific, rapid and simple spectrophotometric method is described. *Procedure*—Dilute a suitable wt. of oil (varying from 20 mg for lemongrass oil to 400 mg for sweet-orange oil) to a known vol. (25 ml for lemongrass, lime and lemon oils and 10 ml for grapefruit and orange oils) with the reagent soln. (dissolve 1 g of barbituric acid in 20 ml of water by gentle warming and dilute the soln. to 100 ml at 25° with anhyd. ethanol), and maintain at 25° for 40 min. Dilute a 1-ml aliquot to 200 ml with anhyd. ethanol (for lemongrass oil), or a 2-ml aliquot to 50 ml (for other oils), and measure the extinction at 336 mμ against a reagent blank of a similarly diluted vol. of the reagent soln. Correct the extinction for that of the oil when similarly diluted with anhyd. ethanol, and from the corrected extinction obtain the amount of citral in the sample by reference to a calibration graph prepared by treating amounts of citral ranging from 10 to 35 mg as for lemongrass oil. Benzaldehyde, cinnamaldehyde and furfuraldehyde do not interfere, although dihydrocitral does.

S. C. Jolly

3847. **Constituents of *Salvia officinalis* L. XI. Analysis of essential oil of sage by gas and thin-film chromatography.** C.-H. Brieskorn and E. Wenger (Pharmaz.-chem. Inst. Univ., Tübingen). *Arch. Pharm., Berlin*, 1960, **293** (1), 21–26.—Fractional distillation of an oil of sage separated 5 terpenes, characterised by conversion into suitable derivatives. Thin-film chromatography on SiO_2 - $CaSO_4$ by Stahl's method indicated the presence of 7 terpenes, identified by colour reactions with vanillin - H_2SO_4 under normal and u.v. light. Fifteen constituents were separated by gas chromatography on a silicone oil - kieselguhr column, with H as the carrier gas. Nine constituents, representing ≃ 8% of the whole, were unidentified.

A. G. Cooper

3848. **Determination of *p*-phenylenediamine in hair-dyes.** A. van de Pol (Lab. Keuringsd. v.

Waren, Nijmegen, Netherlands). *Chem. Weekbl.*, 1960, **56** (2), 21–22.—The method described in "Methods of Analysis, A.O.A.C.", 1955, yields low and poorly reproducible results and has therefore been modified. *Procedure*—To 10 ml of 5% NaClO soln. and 1 g of $NaHCO_3$ in a separating-funnel add a soln. of *p*-phenylenediamine containing 10 to 80 mg. Extract the dichlorimine formed with two 25-ml portions of $CHCl_3$. Transfer the combined extracts to another separating-funnel and wash first with 20 ml of 20% $Na_2S_2O_3$ soln. and then with 10 ml of H_2O. Extract a third time with 25 ml of $CHCl_3$, wash with 10 ml of 20% $Na_2S_2O_3$ soln. and then with 10 ml of H_2O. Combine the washed $CHCl_3$ soln., add 50 ml of H_2O containing 1 g of KI, and 3 ml of 38% HCl. Shake vigorously for 1 min. Titrate the iodine formed with 0·1 *N* $Na_2S_2O_3$, with continuous shaking, adding starch towards the end-point. M. J. MAURICE

3849. **Determination of methyl and phenyl groups in methylphenylsiloxane polymer by NMR spectroscopy.** Tsutomu Kubota and Tsutomu Takamura (Matsuda Res. Lab., Tokyo Shibaura Electric Co., Kawasaki). *Bull. Chem. Soc. Japan*, 1960, **33** (1), 70–73 (in English).—Proton spin resonance spectra are recorded for the three binary mixtures benzene - dioxan, benzene - hexamethylsiloxane, and dioxan - *cyclo*octaphenyltetrasiloxane. In all the systems the peak area due to the resonating proton of the methyl or phenyl group was found to be directly proportional to the number of protons giving rise to the peaks of the respective groups, over a wide range of recording conditions. The determination of methyl and phenyl groups in methylphenylsiloxane polymer is carried out by the use of dioxan as an internal standard. The polymer is mixed with dioxan and the spectrum of the mixture is recorded, the number of each group being then calculated from the appropriate peak area. The results are in good agreement with those obtained by i.r. spectral analysis. I. JONES

3850. **Methods of testing plastics. Part 4: Analytical methods and viscosity in solution.** British Standards Institution (2 Park St., London, W.1). B.S. 2782 : Part 4 : 1958. Amendment No. 4 (28.3.60). 7 pp.—Additional methods are given for viscosity of polyamide resin in formic acid solution and in *m*-cresol solution, for butyl rubber content of "low density" polyethylene compounds, and for phenolic antioxidant content of polyethylene (diazo method).

3851. **Chromatography as a modern aid in the analysis of plastics.** E. Schröder. *Rev. Chim., Bucharest*, 1960, **11** (1), 39–44.—A comprehensive résumé of the applications of chromatography in this field is given. H. SHER

3852. **Volumetric determination of *iso*phthalic and other dicarboxylic acids in modified alkyd resins.** G. G. Esposito and M. H. Swann (Coating and Chem. Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 49–50.—*iso*Phthalic acid (**I**) is isolated as its dipotassium salt by heating a benzene soln. of the resin sample (containing 0·05 to 0·15 g of **I**) under reflux for 1·5 hr. with 200 ml of 0·5 *N* methanolic KOH. The soln. is then diluted with benzene and cooled, and the ppt. is collected in a crucible of coarse porosity, washed with benzene - ethanol (2:1) (150 ml) and dried. Other acids are isolated in a similar fashion, with 60 ml of *N* KOH and heating under reflux for only 1 hr. The salt is washed through the filter into a flask with warm ethanediol (10, 10 and 5 ml), and finally with 100 ml of 0·024 *N* HCl in ethanol. *m*-Cresol purple indicator (0·025 g in 100 ml of abs. ethanol) (3 ml) is added and, if the soln. is not red, *N* HCl is added until a red colour appears. The soln. is agitated for 1 min. and then titrated with 0·2 *N* KOH in methanol. The vol. of titrant used when the colour changes from red to yellow and again when a violet colour appears is recorded. The amount (%) of dicarboxylic acid is calculated from an equation. Results are comparable with those from the u.v. method and the procedure is more rapid and requires no special equipment. S. M. MARSH

3853. **Methods of testing rubber latex. Part 2: Chemical and physical tests.** British Standards Institution (2 Park St., London, W.1). B.S. 1672: Part 2: 1954. Amendment No. 2 (23.2.60). 6 pp.—Methods are given for the determination of the density and of the volatile fatty acid number of latex.

3854. **Condensed tannins. III. Isolation and estimation of (−)-7:3′:4′:5′-tetrahydroxyflavan-3-ol, (+)-catechin and (+)-gallocatechin from black-wattle-bark extract.** D. G. Roux and E. A. Maihs (Leather Ind. Res. Inst., Rhodes Univ., Grahamtown, S. Africa). *Biochem. J.*, 1960, **74** (1), 44–49.—The concn. of the catechins in fresh bark extracts and in their tannin fractions is determined by paper chromatography in conjunction with the measurement of max. colour density of the spots with a densitometer. The two-way chromatograms are run by the ascending method in water-saturated *sec.*-butyl alcohol. After drying, the papers are sprayed with ammoniacal $AgNO_3$ soln. or with a tetrazotised benzidine reagent, and the intensity of the coloured spots is measured. J. N. ASHLEY

3855. **Polarographic determination of nitroglycerin.** A. F. Williams and D. Kenyon (Research Dept., I.C.I., Ltd., Nobel Div., Stevenston, Ayrshire, Scotland). *Talanta*, 1959, **3** (2), 160–171 (in English).—The nitroglycerin is extracted from the explosive with diethyl ether, the extract is evaporated to dryness and the residue dissolved in methanol. Polarograms of this soln. made with a cathode-ray polarograph show 3 waves (−0·25 V, −0·45 V and −0·75 V) instead of the single wave obtained with a conventional polarograph. If no interfering substances are present, as with some propellents, the concn. of nitroglycerin is obtained from the wave height at either −0·25 V or −0·75 V. Blasting explosives and some propellents contain ingredients which interfere with the wave at −0·75 V. A correction must be made if dibutyl phthalate is present. The accuracy is ±2%. The approx. compositions of common types of explosives are given. G. BURGER

3856. **Application of the cathode-ray polarograph to the analysis of explosives. The determination of mercury fulminate.** J. Hetman (Southern Instruments, Ltd., Camberley, Surrey, England). *Talanta*, 1959, **3** (2), 127–130 (in English).—Mercury fulminate in explosive primers can be determined polarographically in soln. in a mixture of pyridine and *N* KNO_3. Correction for interference by Cu in known low concn. can be made with the aid of

calibration graphs. Other common constituents of primers do not interfere; interference from CN^- can be overcome by working with derivative current.
G. BURGER

See also Abstracts—**3603**, Titration of quinol. **3744**, Analysis of Fischer - Tropsch catalysts. **3942**, P in org. compounds. **3972**, Determination of org. bases. **4019**, Determination of pentachlorophenol. **4034**, **4035**, Reactions of org. P compounds. **4048**, Separation of isomers of nitro compounds. **4052**, Location of phenols and aromatic amines on chromatograms. **4059**, Determination of methane. **4087**, "Whiteness" of paints, papers, textiles, etc. **4089**, Burner for combustion of large samples.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

3857. **Rapid method for the determination of water in serum.** A. Macdonald, J. S. Pomeroy and M. H. Gardner (Andrew Yeomans Mem. Res. Lab., Veterans Admin. Centre, White River Junction, Vt., U.S.A.). *Amer. J. Clin. Path.*, 1959, **31** (6), 563–564.—Fresh serum (2 ml) is transferred to a weighing bottle and the water content is determined by drying for 3 hr. under an i.r. lamp. The results agree with those obtained by oven-drying for 72 hr.
P. NICHOLLS

3858. **Infra-red analysis of blood serum, red blood cells and other body fluids.** R. D. Stewart, D. S. Erley, N. E. Skelly and N. Wright (Dow Chemical Co., Midland, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (4), 644–658.—A technique is described for the i.r. examination of body fluids in the 6·7 to 10-μ region with a BaF_2 cell and water or (for pathological samples) the appropriate normal fluid as the reference material. The method is rapid and 2 drops of sample are required, although preliminary concentration is required for dilute specimens. The spectra of 29 samples are presented and the differences between normal and abnormal samples and the potentialities of the method are discussed.
W. H. C. SHAW

3859. **Determination of tritium in biological material.** H. I. Jacobson, G. N. Gupta, C. Fernandex, S. Hennix and E. V. Jensen (Chicago Univ., Ill., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (1), 89–93.—In the method described, the dried blood or tissue sample is converted into water, CO_2 and N by heating with Cu and CuO at 650° in a sealed glass tube. The tube is then broken in an evacuated apparatus and the tritiated water is allowed to distil into a cold trap containing a little H_2O which acts as a carrier. The distillate is then washed with 96% ethanol into a scintillation counting soln. for radioactivity measurement.
W. H. C. SHAW

3860. **Determination of carbon-14 and tritium in blood and other whole tissues. Liquid scintillation counting of tissues.** R. J. Herberg (Lilly Res. Lab., Indianapolis, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 42–46.—Dissolve the sample (< 0·4 ml of whole blood or 100 to 500 mg of wet heart, kidney, liver, spleen, lung or muscle tissue) in *M* methanolic Hyamine hydroxide (prepared from Hyamine 10X crystals) (*cf.* Passmann *et al.*, *Ibid.*, 1956, **28**, 484) or 0·5 *M* ethanolic KOH; shake at 50° or 60° for 24 hr. if necessary and cool. At the same time prepare a tissue background. Oxidise coloured soln. with 30% aq. H_2O_2. Add 10 to 15 ml of either a toluene soln. containing 0·5% of 2:5-diphenyloxazole (**I**) and 0·01% of 1:4-di-(5-phenyl-2-oxazolyl)benzene (**II**) or toluene (500 ml) - dioxan (500 ml) - methanol (300 ml) - naphthalene (104 g) - **I** (6·5 g) - **II** (0·13 g). Acidify the soln. with aq. HCl and count. The method is particularly suitable for the assay of large numbers of samples.
A. R. ROGERS

3861. **Simple test for the presence of metals in biological materials.** C. Milstein (Dept. of Biochem., Tennis Court Rd., Cambridge, England). *Nature*, 1960, **185**, 386–387.—Dissolve the sample of protein (< 1 mg) in 0·003 *M* tri(hydroxymethyl)-methylamine hydrochloride buffer (pH 7·5) (1 ml) and measure the extinction at 253 mμ against a blank; add 0·0025 *M* 8-hydroxyquinoline (0·02 ml) to each soln., mix and again measure the extinction at 253 mμ. The increase of extinction is proportional to the concn. of metal ions. The sensitivity decreases in the order Cu^{2+}, Zn^{2+}, Al^{3+}, Mn^{2+} and Mg^{2+}; Ca^{2+} and Ba^{2+} give no peak. As an example, 0·06 mole of Cu^{2+}, 0·2 mole of Zn^{2+} or 2 moles of Mn^{2+} per mole of phosphoglucomutase gives an increase of extinction of $\simeq$ 0·040 per mg of sample.
A. R. ROGERS

3862. **A micro-method for the estimation of magnesium.** W. H. P. Lewis (Biochem. Dept., Fountain Hospital, London). *J. Med. Lab. Technol.*, 1960, **17** (1), 32–35.—Serum (0·1 ml) is mixed with water (0·65 ml) in a centrifuge tube and 20% trichloroacetic acid (0·5 ml) is added drop by drop. After standing for 15 min., the tube is centrifuged for 10 min. The supernatant liquid (1·0 ml), 0·1% poly(vinyl alcohol) soln. (0·5 ml) and 0·01% Titan yellow soln. (0·5 ml) are mixed in a tube and 15% NaOH soln. (1·0 ml) is added. The extinction is read at 560 mμ in a spectrophotometer with a 4-cm light path and micro cells of approx. 2 ml capacity. Blank and standard estimations are carried out in parallel. The standard soln. contains 2 μg of Mg in 0·1 ml. For red-cell magnesium the packed cells (0·05 ml) are washed into water (0·8 ml) and 20% trichloroacetic acid (0·5 ml) is added. After centrifugation the supernatant liquid (1·0 ml) is treated as above, the standard soln. containing 7 μg of Mg in 0·1 ml.
R. A. BRENAN

3863. **Magnesium-28 studies of the molybdovanadate method for magnesium.** J. K. Aikawa and E. L. Rhoades (Dept. of Med., Univ. of Colorado Sch. of Med., Denver). *Amer. J. Clin. Path.*, 1959, **31** (4), 314–315.—With ^{28}Mg as tracer, a study was made of the method of Simonsen *et al.* (*J. Biol. Chem.*, 1947, **169**, 39) for the determination of Mg in serum and urine. Calcium was completely pptd. within 5 min. and the adsorption of Mg on the ppt. was a minimum. The pptn. of Mg as $MgNH_4PO_4$ was complete within 30 min.
P. NICHOLLS

3864. **Rapid complexometric titration of serum calcium.** H. C. McAllister, jun., and C. L. Yarbro (Dept. of Biochem. and Nutr., Univ. of N. Carolina Sch. of Med., Chapel Hill, U.S.A.). *Clin. Chem.*, 1960, **6** (1), 52–56.—The method of Yarbro and Golby (*Anal. Abstr.*, 1958, **5**, 3076) is adapted to the determination of Ca on 0·2 to 2·0-ml aliquots of serum.
H. F. W. KIRKPATRICK

3865. **Evaluation of a micro-method for serum calcium determination with Calcon as indicator.** J. Boxer (Govt. Hosp. "Rambam," Haifa, Israel). *Clin. Chim. Acta*, 1960, **5** (1), 82–83.—To 2 ml of a soln. prepared freshly before use by adding 5 drops of Calcon (C.I. Mordant Black 17) soln. (0·5% in methanol) to 50 ml of 0·3 *N* NaOH and adjusting to a pure blue colour with EDTA soln. add 0·1 ml of serum. Prepare a second tube similarly and a standard using 0·1 ml of soln. containing 0·016% of Ca. Let the tubes stand for 5 min. then place in a water bath at 60° for 2 min. and titrate, with constant shaking, with 0·01 *M* EDTA until the colour matches a colour blank prepared by adding excess of EDTA soln. to one of the tubes containing the serum. To sharpen the colour change, Mg is added to the standard Ca soln. (0·02 ml of saturated $MgCl_2$ soln. in 25 ml of standard soln.).

H. F. W. KIRKPATRICK

3866. **Survey on the application of visual indicators for the chel[at]ometric calcium determination in serum.** F. S. Sadek and C. N. Reilley (N. Carolina Univ., Chapel Hill, U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (4), 621–629.—From statistical comparisons of results for calcium in artificially prepared serum the chelatometric methods are preferred for rapidity and accuracy over the oxalate - $KMnO_4$ titration method and its modifications. The performances of eight metallochromic indicators for use in the determination on normal sera are evaluated, and their relative merits are discussed.

W. H. C. SHAW

3867. **Separation, estimation and analysis of calcium soaps in human faeces.** H. G. Sammons and S. M. Wiggs (Metab. Res. Unit, Little Bromwich Gen. Hosp., Birmingham, England). *Clin. Chim. Acta*, 1960, **5** (1), 141–145.—*Separation*—An aliquot (10 ml) of a 24-hr. collection of faeces homogenised with H_2O to 1 litre is shaken in a separating-funnel with ether (30 ml). Calcium soaps are dispersed in the ether layer and the aq. layer is run off. The ether is washed with a little H_2O, the washings and the residue are combined and extracted with ether as before; 3 extractions are usually sufficient. The ether extracts are centrifuged at 3000 r.p.m. for 10 min. and the supernatant ether layer is poured off; the soaps are washed twice with ether and weighed when residual ether has evaporated. *Analysis*—The soaps are heated for 30 min. on a boiling-water bath with excess of 2 *N* HCl, then cooled and the fatty acids are extracted with light petroleum. The aq. layer is made up to known vol. and the Ca determined by the method of Henly and Saunders (*Analyst*, 1958, **83**, 584). The petroleum soln. is evaporated at reduced pressure in oxygen-free N and the fatty acids are weighed. The preparation and chromatography of the methyl esters of the fatty acids are also described.

H. F. W. KIRKPATRICK

3868. **Micro-method for the determination of calcium and magnesium in general biological material.** G. Hunter (Cowley Road Hospital, Oxford, England). *Analyst*, 1960, **85**, 12–20.—The calcium and magnesium are pptd. together as phosphates either from a soln. of the ash of the sample or from an extract with trichloroacetic acid. The ppt. is dissolved in *N* HNO_3 and interfering metals are removed by addition of a soln. of Na diethyldithiocarbamate and extraction with CCl_4. The aq. liquid can often be examined directly for Ca, and Ca plus Mg, with murexide and Eriochrome black T as indicators, by the method previously described (*Ibid.*, 1958, **83**, 93; 1959, **84**, 24). Calcium and magnesium are quant. recoverable at concn. of 7×10^{-4} and $2{\cdot}4 \times 10^{-4}$ mole per litre, respectively. Results of the application of the method to a variety of biological materials are given, and a simply constructed device for the initial comminution of the sample is described.

A. O. JONES

3869. **Simultaneous determination of strontium and calcium in urine and serum by flame spectrophotometry.** G. De Angelis and G. Mazzuoli (Ist. Chim. Anal., Univ. Roma, Italy). *Ital. J. Biochem.*, 1959, **8** (6), 319–333 (in English).—Serum (5 ml) or urine (2 ml) is deproteinised with 10% trichloroacetic acid soln. (5 ml), diluting to 10 ml with H_2O if necessary. The filtrate (5 ml) is heated and treated with 4% ammonium oxalate soln. (1 ml) followed by aq. NH_3 soln., the ppt. is allowed to stand overnight and then centrifuged. After being washed with 80% ethanol ($2 \times 0{\cdot}5$ ml) by centrifugation, the ppt. is dissolved in 0·5 *N* HCl (2 ml) and the vol. is made up to 5 ml with H_2O. Flame spectrophotometry is carried out at 423 and 461 mμ, the emission for Ca at 423 mμ being deducted from that at 461 mμ to give a measure of the Sr. Calibration for Ca must be made by pptn. of Ca from standard soln. by the procedure described above and reading at 423 mμ; a standard curve for Sr may be prepared directly from standard soln., reading at 461 mμ, without pptn. Wavelengths of 622 and 681 mμ may be used if the apparatus has no photomultiplier, but the results are less satisfactory.

H. F. W. KIRKPATRICK

3870. **Improved method for the photometric determination of silicon in urine and blood.** Shih-Chung Wang, Shu-Chung Liu and Liang-Wan Tsai (Chinese Acad. of Med. Sci., Peking). *Acta Biochim. Sinica*, 1959, **2** (2), 63–71.—The modified method described is based on the molybdenum-blue reaction, 1-amino-2-naphthol-4-sulphonic acid being used as reducing reagent. The sample is treated with an anion-exchange resin to remove reducing substances normally present in urine. The reaction between silicate and molybdate is then carried out by heating in a boiling-water bath, followed by cooling in an ice bath, in order to achieve satisfactory reproducibility. Interference by phosphate and excess of molybdate is obviated by the use of tartaric acid. Variables, such as time of heating and acidity, are examined. Recovery tests show an error of ±2%. The results by the proposed method agree well with those obtained when samples are previously dried and fused with anhyd. Na_2CO_3.

S. H. YUEN

3871. **Nitric - perchloric acid oxidation for sulphur in plant and animal tissues.** W. M. Shaw (Univ. of Tennessee Agric. Exp. Sta., Knoxville, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (12), 843–847.—The effects of different conditions of time and temp. and digestion vessels in the $HClO_4$ - HNO_3 oxidation of plant materials have been critically examined, and a procedure is described which enables the same digest to be used for the determination of total S as is used for mineral constituents. *Procedure*—Heat gently 1 g of plant or animal sample (or 0·1 g of S-containing compound) in a 100-ml Kohlrausch flask of borosilicate glass with 5 ml each of HNO_3 and $HClO_4$ (70%) until white fumes appear, and maintain the boiling for 1 hr. after the soln. has become pale greenish yellow. Dilute the digest with about 40 ml of water, boil for 15 min., then

filter, and wash the residue with hot water. Determine the SO_4^{2-} in the combined filtrate and washings by any suitable method. Recoveries of S in standard materials were within 2% of theoretical values, and the results were comparable in accuracy and precision with those given by the A.O.A.C. method in which $Mg(NO_3)_2$ is used.

S. C. JOLLY

3872. **Ultra-micro determination of inorganic sulphate.** B. Spencer (Dept. of Biochem., Univ. of Wales, Newport Rd., Cardiff). *Biochem. J.*, 1960, **75** (3), 435–440.—A scaled-down modification of Dodgson and Spencer's benzidine method (*Anal. Abstr.*, 1954, **1**, 1623) is described for the determination of 20 to 400 mμg of SO_4^{2-} in 10-μl samples. The pptd. benzidine sulphate is determined by direct spectrophotometric measurement of benzidine at 248 mμ. Modifications are also described for use with higher concn. of SO_4^{2-} and for 20- and 100-μl samples. The scaled-down method is twice as sensitive as, and much more rapid than, the original method. By the use of the benzidine method, K_2SO_4 is recovered quant. in the presence of various tissue suspensions, sulphatase substrates, and small amounts of certain inorganic ions. The Ba chloranilate method is also scaled down for use with 10-μl samples that contain 0·25 to 2·5 or 2·5 to 25 μg of SO_4^{2-}.

J. N. ASHLEY

3873. **Determination of glutethimide in biological fluids.** L. R. Goldbaum, M. A. Williams and T. Koppanyi (Armed Forces Inst. Path., Washington, D.C., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 81–84.—Shake the sample of blood, plasma or urine (1 to 5 ml) with $CHCl_3$ (25 ml) for 1 min. Filter the $CHCl_3$ layer through paper, wash with 0·5 *N* NaOH (2 × 5 ml) and 0·5 *N* HCl (5 ml) and filter again. Evaporate a 20-ml aliquot of the filtrate just to dryness, dissolve the residue in absolute ethanol (4 ml); mix 3 ml of this soln., containing < 75 μg of glutethimide (**I**), with 0·2 *N* KOH (1 ml) and record the extinction at 235 mμ at 500-sec. intervals for > 2 hr. Correct each extinction by subtraction of the extinction after 10 half-life periods, about 10,000 sec., and plot the logarithms of the corrected extinctions against time; extrapolate to the time of mixing and calculate the initial concn. of **I**. The recovery is $\simeq 100\%$ with an error of $< \pm 5\%$. The washing with alkali removes any 3-methyl-3-phenylglutarimide; 2-phenylglutarimide is not completely removed, but its rate of hydrolysis is about twice that of **I**.

A. R. ROGERS

3874. **Urine colour test for the detection of phenothiazine compounds.** I. S. Forrest and F. M. Forrest (Vet. Admin. Hosp., Brockton, Mass., U.S.A.). *Clin. Chem.*, 1960, **6** (1), 11–15.—A more sensitive reagent for these compounds is proposed, consisting of 5% $FeCl_3$ soln., 20% $HClO_4$ and 50% HNO_3 (1:9:10); 1 ml of this reagent mixed with 1 ml of urine gives an immediate colour reaction. Drug intakes of 5 to 20 mg daily give light pinkish-orange shades, 25 to 70 mg give various shades of pink, 75 to 120 mg give increasingly intense violet shades, and doses of over 125 mg give deep purple colours of increasing opacity. The colour is stable for from 10 sec. with the lowest drug doses to several minutes with the high doses.

H. F. W. KIRKPATRICK

3875. **Specific identification of sulphadiazine in spot analysis.** F. Feigl, V. Anger and V. Gentil (Lab. Prod. Mineral, Min. de Agric., Rio de Janeiro, Brazil). *Clin. Chim. Acta*, 1960, **5** (1), 153–154 (in German).—To a drop of aq. test soln. add a few cg of thiobarbituric acid and heat in a boiling-water bath for 3 to 5 min. Sulphadiazine gives a red to rose colour. Place a drop of this soln. on a filter-paper and examine by u.v. light; a golden-yellow fluorescence is given. The limit of sensitivity is 0·1 μg of sulphadiazine. Other sulpha drugs give no reaction.

H. F. W. KIRKPATRICK

3876. **Organic analysis. XX. Micro-estimation of blood sugar with 5-hydroxy-1-tetralone.** Tsutomu Momose and Yosuke Ohkura (Pharm. Inst., Med. Fac., Univ. of Kyushu, Japan). *Talanta*, 1959, **3** (2), 151–154 (in English).—A soln. of 5-hydroxy-1-tetralone (100 mg) in H_2SO_4 (400 ml) gives a green fluorescence under u.v. light when heated with a soln. of a hexose or of a polysaccharide that contains a hexose unit in the molecule. The intensity of fluorescence is used to determine the sugar concn. in 0·02 ml of blood which has been haemolysed and deproteinised with trichloroacetic acid. The intensity is measured in a fluorimeter calibrated against glucose. Cellulose dust must be rigorously excluded.

G. BURGER

3877. **Influence of peptides, peptones and proteins on the determination of sugar by the Potterat-Eschmann method.** W. Kupferschmid (Lebensmittelchem. u. Chem. Abt., Bezirks-Hyg. Inst., Gera, Germany). *Nahrung*, 1959, **3** (7–8), 754–758.—It is shown that peptides, peptones and proteins interfere significantly with the method of Potterat and Eschmann (*Anal. Abstr.*, 1955, **2**, 1327). These compounds can, however, be largely eliminated by clarification by the Carrez procedure *viz*, treatment of the soln. with 15% $K_4Fe(CN)_6$ soln. (2 ml) and 30% $ZnSO_4$ soln. (2 ml), neutralisation to phenolphthalein with *N* NaOH and filtration. Further preliminary treatment is not usually necessary.

S. M. MARSH

3878. **New method for the examination of melituria. Separation and identification of urinary sugars by means of paper electrophoresis at high potential gradient.** Iwao Iuchi and Susumu Shibata (Yanaguchi Med. Coll., Ube, Japan). *Clin. Chim. Acta*, 1960, **5** (1), 42–47 (in English).—Borate buffer soln. (pH 10·8) is used at two strengths—(*A*) 20·3 g of boric acid is dissolved in 327 ml of aq. *N* NaOH and the soln. is diluted to 2 litres; *B* is prepared as *A* but diluted only to 500 ml. *A* is used for the paper strips and electrode vessels, and *B* for diluting the urine (4 vol. of urine, 3 vol. of buffer). Aliquots (10 μl) of the diluted urine are applied to Whatman No. 1 strips and 23 V per cm and 1·1 mA per cm applied for the first 10 min., and then 70 V per cm and 5 to 7·5 mA per cm for the next 40 min. The strips are dried by gentle heat and immersed in $AgNO_3$ soln. prepared by adding satd. aq. $AgNO_3$ soln. (1 ml) to acetone (200 ml) and adding H_2O dropwise until the ppt. re-dissolves. The strips are dried and sprayed uniformly with *N* NaOH - ethanol (1:1); after some minutes they are dipped in conc. aq. NH_3 - H_2O (1:1) until Ag_2O is removed, washed in running H_2O, blotted on dry paper, and dried by gentle heat. In glycosuria three distinctly separated bands of glucose, uric acid and urea-creatinine are observed. Glucose, fructose, ribose, rhamnose, lactose, maltose, sucrose, glucuronic acid and glucosamine are easily identified by this technique. Sorbose and xylose are difficult to differentiate from glucose, and overlapping occurs between the bands of galactose and fructose, and of ribose and mannose.

H. F. W. KIRKPATRICK

3879. **Deoxy sugars. XXXIII. Paper-chromatographic separation of the hexamethyloses [6-deoxyhexoses] and their 3-O-methyl derivatives.** M. T. Krauss, H. Jäger, O. Schindler and T. Reichstein (Org.-chem. Anst. der Univ., Basel, Switzerland). *J. Chromatography*, 1960, **3** (1), 63–74 (in German).—R_F values are tabulated for 7 solvent systems, the separated compounds being detected by spraying with blue tetrazolium or aniline phthalate. A detailed discussion is given of the effect of stereochemical factors involved in complex formation, with special reference to the use of $Na_2B_4O_7$ soln. as the stationary phase. W. T. CARTER

3880. **Microbiological determination of meso-inositol in blood. Normal and pathological variations.** R. Perlès and M. C. Colas (Lab. Chim. Biol., Fac. de Pharm., Univ. Paris, France). *Clin. Chim. Acta*, 1960, **5** (1), 95–99.—Plasma is dialysed, the dialysate is passed through ion-exchange columns, and the assay carried out by the use of *Neurospora crassa*. H. F. W. KIRKPATRICK

3881. **Ferric chloride test for phenylpyruvic acid in urine.** O. Meulemans (Dept. of Pediatrics, Univ. Utrecht, Netherlands). *Clin. Chim. Acta*, 1960, **5** (1), 152–153 (in English).—The masking effect of phosphates is avoided by the use of a mixture of $MgCl_2$ (11 g), NH_4Cl (14 g) and aq. NH_3 soln. (22·5 ml of 25% aq. NH_3) diluted to 1 litre. To 4 ml of urine add 1 ml of the mixture and filter from the ppt. after 5 min. Acidify the filtrate with 2 drops of 10% HCl and add 1 to 3 drops of 10% $FeCl_3$ soln. A green colour denotes a positive reaction. H. F. W. KIRKPATRICK

3882. **Phenylpyruvic acid in urine.** O. Meulemans (Dept. of Pediatrics, State Univ., Utrecht, Netherlands). *Clin. Chim. Acta*, 1960, **5** (1), 48–53 (in English).—The method of The *et al.* (*Ibid.*, 1957, **2**, 424) is modified. The extinction of the green colour produced with $FeCl_3$ is corrected by measuring the extinction after the colour has faded. This procedure gives increased accuracy and allows the assay of small concn. of phenylpyruvic acid. H. F. W. KIRKPATRICK

3883. **Colorimetric estimation of 4-hydroxy-3-methoxymandelic acid in urine.** M. Sandler and C. R. J. Ruthven (Bernhard Baron Mem. Res. Lab., Queen Charlotte's Matern. Hosp., London). *Lancet*, 1959, **ii**, 1034.—Certain improvements in procedure of the method previously published (*cf. Anal. Abstr.*, 1960, **7**, 1493) are recommended.

3884. **Assay for pantothenic acid in biological fluids.** H. Baker, O. Frank, I. Pasher, A. Dinnerstein and H. Sobotka (Mt. Sinai Hosp., New York, U.S.A.). *Clin. Chem.*, 1960, **6** (1), 36–42.—Microbiological methods are described with *Lactobacillus plantarum* and *Tetrahymena pyriformis*. H. F. W. KIRKPATRICK

3885. **Determination of vitamin B_{12} in blood.** N. V. Myasishcheva (Bacteriolog. Lab., Leningrad Order of the Labour Red Banner Sci. Study Inst. of Blood Transfusion). *Lab. Delo*, 1960, **6** (1), 35–37.—A microbiological method is given for the determination of vitamin B_{12} in blood by the stimulation of the growth of *Escherichia coli*. Bromothymol blue is used as an indicator to follow increase in acidity. The vitamin content is determined colorimetrically by comparison with standard soln. Figures ranging from 75 to 300 μμg of vitamin B_{12} per ml of blood were obtained. A. BURWOOD-SMITH

3886. **Distribution of radioactive and non-radioactive vitamin B_{12} in the dog. [Determination of vitamin B_{12}.]** J. M. Cooperman, A. L. Luhby, D. N. Teller and J. F. Marley (Haematology and Nutr. Lab., Dept. of Pediat., New York Med. Coll., U.S.A.). *J. Biol. Chem.*, 1960, **235** (1), 191–194.—The *Lactobacillus lactis* microbiological assay of Cooperman *et al.* (*Brit. Abstr. C*, 1951, 467) for vitamin B_{12} is improved, so that the assay is completed in 6 hr. instead of 40 hr.; the sensitivity is increased so that as little as 3 μμg of vitamin per ml can be determined. J. N. ASHLEY

3887. **Analysis of inulin.** K. Täufel and K. J. Steinbach (Inst. f. Lebensmittelchem. u. technol., Humboldt Univ., Berlin, Germany). *Nahrung*, 1959, **3** (7–8), 701–711.—A systematic investigation of the reducing sugars and decomposition products obtained in the acid hydrolysis of inulin is described. About 9% less than the theoretical amount of fructose is usually formed, but this loss can be reduced to 6% by using mild acid conditions (0·05% HCl at 70°). The deficit is thought to be caused by incomplete hydrolysis of inulin and by desmolytic degradation of fructose to hydroxymethylfurfuraldehyde. The latter process can be eliminated under carefully controlled conditions and it is evident that it does not contribute to the deficiency of reducing monosaccharide. Reversion, with formation of difructose anhydride, is a possible cause. S. M. MARSH

3888. **Use of *i*sonicotinic acid hydrazide [isoniazid] as a reagent for the determination of certain flavonoids.** C. D. Hawker, H. W. Margraf and T. E. Weichselbaum (Dept. of Surgery, Washington Univ. Sch. of Med., Washington, D.C.). *Anal. Chem.*, 1960, **32** (1), 122–124.—A 0·05% soln. of isoniazid in 0·023% ethanolic HCl and a 0·4% soln. of isoniazid in 0·185% methanolic HCl are suggested as spray reagents for the detection of as little as 5 μg of flavonoids on paper chromatograms. Characteristic yellow fluorescence is given by hydroxyflavone aglycones, flavanones, flavanols and chalcones, but not by flavones and hydroxyflavone glycosides. The reaction can be used in combination with other techniques in a scheme for the identification of various groups of flavonoids. For quant. determination, elute the flavonoid from the paper, evaporate to dryness, heat the residue at 50° for 2·5 hr. with the 0·4% isoniazid reagent, cool the soln. and measure the extinction at 405 mμ within 10 min. against a blank which contains no isoniazid. A. R. ROGERS

3889. **Detection of conjugated methylene-lactones by infra-red spectroscopy.** M. Horák and J. Plíva (Inst. Chem., Czech. Acad. Sci., Prague). *Chem. & Ind.*, 1960, (4), 102.—The conjugation of the methylene double-bond with the lactone carbonyl group is detected by a slight frequency shift ($\simeq$ 7 cm^{-1}) of the carbonyl group. This shift is determined by comparison of the frequency of the carbonyl group of the lactone with that of its dihydro derivative. Data for seven naturally occurring lactones are given. G. P. COOK

3890. **The enzymic synthesis of aryl sulphamates. [Assay of 2-naphthyl sulphamate.]** A. B. Roy (Dept. of Biochem., Univ. of Edinburgh, Scotland).

Biochem. J., 1960, **74** (1), 49–56.—The assay is used to determine the synthesis of 2-naphthyl sulphamate by liver prep. It is based on the removal of free amino compounds by treatment with Zeo-Karb 225 (H^+ form), hydrolysis of the sulphamate with aq. HCl and determination of the resulting 2-naphthylamine by diazotisation and subsequent coupling with thymol. The intensity of the orange-yellow colour is read in a Spekker absorptiometer with Ilford filter 602 (max. transmission at 470 mμ) and the amount of amine is ascertained from a standard graph. J. N. ASHLEY

3891. **The determination of aminophenols and aminobenzoic acids. A study of extraction procedures applicable to biological materials.** S. L. Tompsett (Biochem. Lab., Northern General Hospital, Edinburgh, Gt. Britain). *Anal. Chim. Acta*, 1959, **21** (6), 555–560 (in English).—The effect of pH on the ether extraction of aqueous soln. of *o*- and *p*-aminobenzoic acids, 3-hydroxyanthranilic acid and *o*- and *p*-aminophenols is reported. Some success is reported in the separation of these components by HCl elution from a cation-exchange resin (Dowex 50). T. R. ANDREW

3892. **Tungstenometric method for the determination of uric acid in urine.** L. A. Maĭ (Republican Blood Transfusion Sta., Riga, Latvia). *Lab. Delo*, 1960, **6** (1), 30–32.—The influence of the following variables on the accuracy of the method previously described (*Anal. Abstr.*, 1958, **5**, 4234) has been studied—foreign substances in the urine, the presence of alkalis in the titration soln., variation of pH and time of standing of the titration soln. A. BURWOOD-SMITH

3893. **Fluorimetric determination of adrenaline and noradrenaline.** T. Canbäck and J. G. L. Harthon (Apoteket Ugglan, Stockholm, Sweden). *J. Pharm. Pharmacol.*, 1959, **11** (12), 764–766.—Pharmaceutical preparations of adrenaline (**I**) and noradrenaline (**II**) may contain sulphite as a stabiliser and this must be destroyed before the determination. The method described is essentially similar to that of Crawford and Law (*cf. Anal. Abstr.*, 1958, **5**, 4241). *Procedure*—To an aliquot of the sample containing 25 to 50 μg of **I** or **II** add 0·1 *N* HCl (2 ml), starch indicator (2 drops) and 0·1 *N* iodine drop by drop until a blue colour appears. Add 0·2% As_2O_3 soln. (0·5 ml), dilute with H_2O to 15 ml and mix. To a 5-ml aliquot add phosphate buffer soln. of pH 7 (5 ml) and MnO_2 (100 mg), stopper the tube and shake for 1·5 min., then centrifuge for 1 to 2 min. at 3000 r.p.m. Mix 5 ml of the supernatant liquid with 0·1% ascorbic acid soln. (5 ml), dilute with 1·1 *M* NaOH to 25 ml and measure the fluorescence max. after about 5 min. Correction for background fluorescence is rarely necessary. The method cannot be applied to pharmaceutical preparations that contain procaine and **II**. A. R. ROGERS

3894. **Modification of spectrofluorimetric determination of aminochromes in human plasma.** A. N. Payza and M. E. Mahon (Psychiatric Res. Unit., Dept. of Public Health, University Hospital, Saskatoon, Sask., Canada). *Anal. Chem.*, 1960, **32** (1), 17–19.—The method described previously (*cf. Anal. Abstr.*, 1960, **7**, 1129) has been modified so that it can now be applied to samples of whole tissues. To increase the stability of the reagent blank, ascorbic acid has been omitted from the reagents. Indoles do not interfere. A. R. ROGERS

3895. **Assay of acetylcholine with the isolated semispinalis cervicis muscle of the chick.** C. Tyler (Dept. of Pharmacol., Royal Free Hosp. Sch. of Med., 8 Hunter St., London). *Analyst*, 1960, **85**, 8–11.—The semispinalis cervicis muscle of the chick responds by contracture to acetylcholine and substances with an acetylcholine-like action at the neuromuscular junction. In the method described, these muscles of 2 to 3-week-old chicks are used for the rapid and accurate assay of acetylcholine. The preparation is sensitised to acetylcholine by the addition of the anticholinesterase drug edrophonium chloride to the isolated-organ bath before each addition of acetylcholine. Ten assays of a (2,2) design were made on soln. of known potency. The mean error was ±2·8%, the mean fiducial limits of error were 7·3%, and the mean index of precision was 0·031. A. O. JONES

3896. **Chromatographic method for the estimation of nicotinuric acid and nicotinamide.** K. M. Jones (Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1959, **73** (4), 719–723.—A direct method is described for the determination of nicotinuric acid (**I**) or nicotinamide (**II**) in the presence of large amounts of nicotinic acid. It depends on the separation of **I** or **II** from interfering substances by paper chromatography and measurement of their u.v. absorption after elution from the paper. Linear calibration curves are obtained for 0 to 100 μg of **I** and for 0 to 40 μg of **II**. The error is ±2 μg and the method is specific only in so far as the separation is complete. The chief disadvantage is the long time (18 to 48 hr.) needed for the development of the chromatograms by the descending technique with *n*-butanol satd. with water, but several determinations can be carried out simultaneously. J. N. ASHLEY

3897. **Separation [and determination] of nitrogen-containing phosphate esters from brain and spinal cord by ion-exchange chromatography.** R. W. R. Baker and G. Porcellati (Dept. of Chem. Path., Guy's Hosp. Med. Sch., London, England). *Biochem. J.*, 1959, **73** (4), 561–566.—The method, in conjunction with specific colorimetric procedures, is well suited for the determination of the phosphate esters of choline, ethanolamine and serine in extracts of brain or spinal cord. It depends on the resolution of the aq. extracts on a column of finely divided sulphonated polystyrene resin. Sharp peaks are obtained with each of the various classes of substance, ranging from compounds of relatively small mol. wt. to others that resemble peptides. There is some overlapping of the glycerylphosphoryl and phosphoryl deriv. of ethanolamine with the corresponding choline compounds; in such cases the ethanolamine compounds can be determined by the specific reaction with ninhydrin. J. N. ASHLEY

3898. **Chromatographic methods for the identification of biogenic amines.** J. Awapara, V. E. Davis and O. Graham (Rice Inst. Biology Dept., Houston, Tex., U.S.A.). *J. Chromatography*, 1960, **3** (1), 11–19.—Mono- and di-carboxylic amino acids are separated from amines and basic amino acids on a column of Amberlite CG50, Type 2. The acidic amino acids are eluted with water and the amines with 4 *N* acetic acid. The recoveries of both groups of compounds are from 93 to 111%. The amines are separated by column chromatography on cellulose powder, with butanol - acetic acid - water (4:1:1·6) or ethyl methyl ketone - propionic acid -

water (3:1:1·2) as solvent. The fractions are analysed colorimetrically with ninhydrin, or by measuring the extinction at 279 mμ or by paper chromatography. Since ethyl methyl ketone interferes with the first two methods, paper chromatography is the only method available for analysing the fractions obtained with the second solvent system and it is carried out with the same solvents as in the column chromatography. The amines are detected by ninhydrin and phenolic compounds with diazotised sulphanilic acid. R_F values are given for 26 naturally occurring amines with 4 different solvent systems. W. T. CARTER

3899. **Photometric micro-determination of amino acids in biological fluids with the ninhydrin reaction.** A. Saifer, S. Gerstenfeld and A. F. Harris (Isaac Albert Inst., Jewish Chronic Dis. Hosp., Brooklyn, N.Y., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (1), 131–140.—The method of Yemm and Cocking (*Analyst*, 1955, **80**, 209) is modified, and procedures for the determination of amino-acid N in serum or plasma, cerebrospinal fluid and urine are described. Results for normal and pathological subjects are given. H. F. W. KIRKPATRICK

3900. **Fractionation and estimation of free amino acids in serum.** E. R. Cook and M. Luscombe (Rheumatism Res. Unit, Royal Nat. Hosp. for Rheumatic Diseases, Bath, England). *J. Chromatography*, 1960, **3** (1), 75–84.—The acids are isolated by adsorption on a column of Zeo-Karb 225 (H^+ form) and eluted with 10% aq. NH_3. They are then fractionated into 6 groups by paper electrophoresis at 1350 V in *N* acetic acid for 2·5 to 3 hr. The groups are located by u.v. fluorescence after immersion in 0·1% *o*-coumaric acid in acetone and then separated as individual acids by descending paper chromatography, with a solvent mixture containing *n*-butanol, ethanol, ethyl acetate, water and acetic acid. The separated acids are determined by spraying the paper with a lactic acid - ninhydrin soln. in ethanol, after which the spots are cut out and eluted with ethanolic $CdSO_4$ soln. The extinctions of the pink soln. are then measured in a Spekker photometer, with an Ilford No. 604 filter. The pink colour is stable overnight, and is more sensitive than the normal ninhydrin blue. Recoveries of 14 amino acids added to serum and from synthetic mixtures averaged 86%. W. T. CARTER

3901. **Separation of amino acids from complex biological media. V. Description of a combination of chromatographic and electrophoretic methods.** G. Biserte, T. Plaquet-Schoonaërt, P. Boulanger and P. Paysant (Lab. de Chim. Biol., Fac. de Méd. et de Pharm., Lille, France). *J. Chromatography*, 1960, **3** (1), 25–47 (in French).—A preliminary separation is obtained by paper electrophoresis at pH 3·9 and a potential of 400 V for 4 hr. This separates the compounds into three main groups which are then treated separately. The first group (consisting of acidic amino acids and other organic acids) is further separated by a two-dimensional combination of electrophoresis in one direction at pH 3·9 and 600 V for 8 hr. followed by chromatography in the second direction with *n*-butanol - acetic acid - water (4:1:5). The second group is eluted from the first electropherogram and consists of neutral amino acids together with glucose, urea and creatine. It is further separated by electrophoresis at pH 2·9 and 400 V for 18 hr. followed by chromatography in the second direction with the above solvent. The third group, consisting of basic amino acids and amines, is also eluted from the first electropherogram and separated by electrophoresis at 400 V for 15 hr. at pH 11·7 and 6·5. The separated compounds are located by normal spraying methods but improved results are obtained by using only volatile solvents and buffer soln. With complex biological material it may be necessary to carry out analyses before and after hydrolysis. W. T. CARTER

3902. **Further contribution to separation of amino acids on ion-exchange columns.** J. Schormüller and E. Hofmeister (Inst. f. Lebensmittelchem. u. -technol., Tech. Univ., Berlin). *Z. Lebensmitt-Untersuch.*, 1959, **111** (1), 20–23.—The method of Ishii (*Anal. Abstr.*, 1957, **4**, 4091) gives results accurate to within ±3% in the separation of arginine, histidine, lysine, tryptophan and ammonia on Amberlite XE-64 with the use of a single citrate - phosphate buffer at pH 6·0 for elution. The method is more convenient than that of Moore and Stein. A method is also described for the analysis of mixtures of hydroxyproline and aspartic acid (obtained in eluates from Dowex 50-X8) by a calculation based on the extinctions, at two different wavelengths, of their reaction products with ninhydrin. P. S. ARUP

3903. **Anomalous reactions in the amino-nitrogen determination. VIII. Some anomalous amino acids.** G. Kainz and F. Kasler (Chem. Inst., Univ. Wien, Austria). *Mikrochim. Acta*, 1960, (1), 62–71 (in German).—Chromatographic analysis of the gas evolved on treating nine amino acids with 30% $NaNO_2$ soln. at 80° indicated that each acid produced at least 0·33 mole of CO_2 and widely varied amounts of N and N_2O. Reaction mechanisms are proposed for seven of the acids in which the formation of a nitrolic acid takes place simultaneously with the formation of the hydroxyl compound during deamination. With α-amino acids, CO_2 is also liberated at this stage. At elevated temperatures the nitrolic acid reacts with HNO_2 with the production of N and N_2O and the corresponding carbonyl compound. In some cases secondary side-reactions occur, owing to the intermediate formation of malonic acid, the presence of phenolic groupings, or the oxidation of disulphide groups by HNO_2. W. T. CARTER

3904. **Infra-red spectra of deuterated α-amino acids $NH_3^+CDRCOO^-$. Assignment of the absorption bands of α-alanine.** Shigeko Suzuki, Tairo Ohshima, Nobuo Tamiya, Kunio Fukushima, Takehiko Shimanouchi and San-Ichiro Mizushima (Fac. Sci., Tokyo Univ., Hongo, Japan). *Spectrochim. Acta*, 1959, (11), 969–976.—The preparation of C-deuterated α-amino acids by electrolytic reduction and enzymic methods is described. Comparison of the infra-red spectra of these and the N-deuterated and non-deuterated compounds has led to the assignment of the infra-red absorption bands of all of them and of those of α-alanine. E. G. CUMMINS

3905. **Notes on a modification of the Neuman and Logan method for the determination of hydroxyproline.** A. A. Leach (Brit. Gelatine and Glue Res. Ass., 2a Dalmeny Av., London, England). *Biochem. J.*, 1960, **74** (1), 70–71.—The modified method combines stages 1 and 2 of the original Neuman and Logan method (*Brit. Abstr. C*, 1950, 412). The oxidation of the hydroxyproline with H_2O_2 in the presence of alkaline $CuSO_4$ is carried out at 40°

and is completed before the total destruction of the excess of H_2O_2 has occurred. The modified method gives greater reproducibility, and colour yields are reproducible over a long period. J. N. ASHLEY

3906. **Spectrophotometric determination of tryptophan by the method of Roth and Schuster: some sources of error.** I. Larsen (Dept. of Soil Fertility and Plant Nutrition, Royal Vet. and Agric. Coll., Copenhagen, Denmark). *Nature*, 1960, **185**, 316–317.—The colorimetric method of Roth and Schuster (*Angew. Chem.*, 1939, **52**, 149) has been studied spectrophotometrically. Oxides of nitrogen should be removed by aspiration with air before measurement of the extinction, which should be made at a wavelength longer than 440 mμ to avoid interference by certain vegetable constituents. Even at 450 mμ the presence of lignin leads to high results. A. R. ROGERS

3907. **Excretion of a dose of tryptophan for the detection of vitamin-B6 deficiency.** G. Kupke and A. Knapp (Inst. f. Ernährung, Potsdam-Rehbrücke). *Nahrung*, 1959, **3** (5–6), 402–413.—It is shown that the detection of pyridoxine deficiency by determination of the amount of urinary xanthurenic acid after administration of a dose of tryptophan must be supplemented by determinations of urinary kynurenine (**I**) and 3-hydroxykynurenine (**II**). *Procedures*: (*i*) *Chromatographic separation*—The urine (fresh) (0·2 ml) is chromatographed on S. & S. 2043b paper with methanol - *n*-butanol - light petroleum - water (2:1:1:1) for 10 to 12 hr. The paper is then dried at room temp. and examined under u.v. light; **I** gives a spot ($R_F \simeq 0{\cdot}4$) with a light bluish fluorescence and **II** gives one ($R_F = 0{\cdot}3$) with a lemon-yellow fluorescence. Standard soln. (up to 30 μg) of **I** and **II** are chromatographed simultaneously. The spots of **I** are cut out and eluted with water (3 to 4 ml) thrice for 20 min. at 95° to 100°, and the combined eluates are made up to 10 ml. The spots of **II** are similarly treated at 20° to 25°. (*ii*) *Determination of* **I**—The eluate (10 ml) is cooled to 0° and treated with 0·2% $NaNO_2$ soln. in 0·1 *N* HCl (1 ml) and, after 15 min., with 0·2% ethanolic *N*-ethyl-1-naphthylamine soln. (2 ml) and immediately shaken, then set aside for 1 hr. at 0°. *iso*Amyl alcohol (1 ml) and ethanol (10 ml) are added, and the mixture is shaken and set aside for a further 2 hr. The extinction is then read at 540 mμ in a 2-cm cell, and compared with the standards. (*iii*) *Determination of* **II**—The eluate (10 ml) is treated with satd. Na_2CO_3 soln. (5 drops) and 0·1 ml of diazotised sulphanilic acid soln. (dissolve 0·43 g of sulphanilic acid in 50 ml of 0·1 *N* HCl, and dilute to 100 ml with water; dissolve 0·2 g of $NaNO_2$ in 100 ml of water; mix 1 ml of each soln. and dilute to 20 ml with water). After exactly 15 sec. denatured ethanol (2 ml) is added and the extinction is read at 500 mμ in a 2-cm cell, and compared with the standards. S. M. MARSH

3908. **Polarographic determination of α-methyl-DL-cystine.** R. J. Thibert and R. M. Ottenbrite (Essex Coll., Assumption Univ. of Windsor, Ontario, Canada). *Anal. Chem.*, 1960, **32** (1), 106–107.—The diffusion current is directly proportional to the concn. of α-methyl-DL-cystine in the range 0·5 to 2·0 m*M* for soln. in 0·1 *N* HCl, in the presence of thymol as a maximum suppressor. The system is not reversible. The influence of change of temp., pH and concn. of thymol has been studied. A. R. ROGERS

3909. **Radioautographic detection of metabolites of DL-[^{35}S]cystine.** D. Cavallini, C. De Marco, B. Mondovì and L. Tentori (Inst. Biol. Chem., Univ. Modena, Italy). *J. Chromatography*, 1960, **3** (1), 20–24.—Liver extracts and urine from rats fed on DL-[^{35}S]cystine were subjected to two-dimensional chromatography with water-satd. phenol and water - collidine - lutidine. The separated compounds were located by the preparation of radioautograms and also by spraying with ninhydrin. Of the 12 compounds detected, 5 were identified as taurine, hypotaurine, thiotaurine, thiazolidinecarboxylic acid and cystine sulphonate. W. T. CARTER

3910. **The determination of blood glutathione.** W. W. Kay and K. C. Murfitt (Mental Hosp. Group Lab., West Park Hosp., Epsom, Surrey, England). *Biochem. J.*, 1960, **74** (1), 203–208.—The lysed blood is de-proteinised with trichloroacetic acid, then neutralised with NaOH and treated with alloxan. The reduced glutathione reacts with the alloxan to give a substance with an absorption band at 305 mμ. Extinctions are measured spectrophotometrically. The method, which has not been extended to tissues, readily detects 15 μg of reduced glutathione, and can be used to estimate it in 0·2 ml of blood. β-Alanine, methionine, and cysteine inhibit the reaction, while citrate, glycine and other α-amino acids are activators. J. N. ASHLEY

3911. **Method for the determination of guanidinoacetic acid and arginine in biological fluids.** C. Wu (Mich. Univ. Med. Sch., Ann Arbor, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 461–470.—Extracts or dilutions of biological tissues and fluids containing 0·05 to 0·2 μmole of arginine and of guanidinoacetic acid are chromatographed on Amberlite CG50 (Na^+) resin, which retains arginine only. The eluate is then passed through a column of Nalcite HCR-8, which retains the guanidinoacetic acid. Each column is then eluted separately with 0·5 *M* Na acetate and the two compounds are determined colorimetrically on aliquots of the eluates by the Sakaguchi reaction. Recovery of added compounds from urine, plasma and kidney extracts is 96 to 104%. W. H. C. SHAW

3912. **The estimation of aminoacetone and δ-aminolaevulic acid.** W. H. Elliott (John Curtin Sch. of Med. Res., Aust. Nat. Univ., Canberra, A.C.T., Australia). *Biochem. J.*, 1960, **74** (1), 90–94.—The sample of aminoacetone (0·05 to 0·5 μmole) or δ-aminolaevulic acid (0·05 to 0·8 μmole) in water (2·5 ml) is mixed with saturated aq. picric acid (0·25 ml) and cooled to 0°; 5 *N* NaOH (0·5 ml) at 0° is added and the mixture is kept at 0°. After 6 min. or 14 min. (for aminoacetone and δ-aminolaevulic acid, respectively), 4 *N* HCl (1·75 ml) is added and the mixture is brought to room temp. After a further 10 min. the extinction is measured at 495 mμ. The colour fades at the rate of 2% per 10 min. at room temp. The method is less sensitive than that of Mauzerall and Granick (*Anal. Abstr.*, 1956, **3**, 2528), but can be used under conditions when the latter method is inapplicable. It has the additional advantage that, when combined with a simple resin treatment, only aminoketones, among biologically occurring compounds, will react. The aminoacetone and δ-aminolaevulic acid are readily separated on Amberlite IRC-50 buffered at pH 4·7 to 5·0 with Na acetate; the aminoketone is retained by the resin and can be eluted with aq. HCl.

They can also be separated on paper by the system ethanol - *N* acetic acid - pyridine - water (95:10:3:3, by vol.) and by paper electrophoresis at pH 4·0 to 6·5. J. N. ASHLEY

3913. **Amperometric titration of albumin in blood serum by copper(II).** I. M. Kolthoff, B. R. Willeford, jun., and D. Singh (Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (1), 92–95 (in English).—Albumin in human blood serum is titrated amperometrically with 0·048 *M* $CuSO_4$. The supporting electrolyte is 0·1 *M* aq. NH_3 - 0·1 *M* NH_4NO_3 with a pH of 9·2, and a rotating platinum electrode is used at a potential of 0·4 V *vs.* the S.C.E. The results are a little lower than those obtained by pptn. in Na_2SO_3 soln. H. N. S.

3914. **Method for the electrophoretic separation of serum proteins on a starch gel.** V. M. Rodinov, Zh. A. Antokolskaya, A. V. Chudinovskikh and L. A. Loboda (Inst. of Biolog. and Med. Chem., Moscow). *Lab. Delo*, 1960, **6** (1), 23–25.—An apparatus is described in which serum proteins are separated in a column of starch gel (7% of starch in a barbitone buffer of pH 8·6 and ionic strength 0·025). The electrolyte is 0·9% NaCl soln. and electrophoresis is carried out for 18 to 20 hr. at 200 to 250 V and 70 to 100 mA. After electrophoresis the starch column is separated into discs, each of which is weighed and treated with an equal quantity of extracting soln. (50% of methanol in 8% Na_2CO_3 soln.). The starch settles out and the clear liquid is centrifuged before the protein concn. is measured by the method of Lowry *et al.* (*J. Biol. Chem.*, 1951, **193**, 265). A. BURWOOD-SMITH

3915. **Rapid micro-electrophoresis of serum total proteins and lipoproteins.** B. Zak, T. L. Jarkowski and L. A. Williams (Dept. of Path., Wayne State Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Amer. J. Clin. Path.*, 1959, **31** (6), 559–562.—Serum proteins and lipoproteins are separated by zone electrophoresis at 250 V, with dilute agar gel (175 mg per 100 ml of barbitone buffer, ionic strength 0·05, pH 8·6) on a tissue slide, in 25 and 10 min., respectively. Amido black (C.I. Acid Black 1) is used as the stain for total protein and Oil red O (C.I. Solvent Red 27) for lipoprotein. P. NICHOLLS

3916. **Gas-counting method for determination of carbon-14 of proteins labelled with both carbon-14 and iodine-131.** T. Salo and B. Blair (Tennessee Univ., Knoxville, U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (1), 10–15.—Two methods are described. The first, for total C, involves combustion of the sample by the Van Slyke procedure with modified reagents to prevent contamination of the $^{14}CO_2$ with ^{131}I. The vol. of CO_2 is measured and the gas is then transferred to a gas-counting apparatus for measurement of the radioactivity due to $^{14}CO_2$. In the second method only α-carboxyl ^{14}C is determined. After preliminary hydrolysis, the resulting amino acids are decarboxylated by treatment with ninhydrin, and the CO_2 produced is measured and counted as described above. The errors for the methods are $\simeq$ 4% and $\simeq$ 6%, respectively. W. H. C. SHAW

3917. **Method for the determination of glycoproteins in blood serum.** R. A. Joffe (Central Inst. for the Advancement of Med., Moscow). *Lab. Delo*, 1960, **6** (1), 11–15.—Chromatography is used for this determination in blood serum from normal and tuberculous subjects. After heating to 80° to 90°, the chromatograms are immersed for 5 min. in HIO_4 soln. (1·2 g of HIO_4 in 30 ml of H_2O to which is added 15 ml of *M* Na acetate soln. in 100 ml of ethanol), and then for 15 min. in bromine water. The strips are then stained by immersion for 30 min. in 0·1% toluidine blue soln., washed to remove the excess of dye, fixed for 5 min. in 4% ammonium molybdate soln. and dried at 100°. The five bands on the strip correspond to the five serum fractions. Quantitative determination of the glycoproteins is carried out either by the method of Benhamon *et al.* (*Presse Méd.*, 1954, **62**, 651) or by extraction of the dye with 20% H_2SO_4 and colorimetric evaluation. A. BURWOOD-SMITH

3918. **Distribution of mucoprotein in gelatins and fractionated gelatins. [Determination of mucoprotein.]** A. Courts (Brit. Gelatine and Glue Res. Assoc., 2a Dalmeny Av., London, N.7, England). *Biochem. J.*, 1959, **73** (4), 600–603.—The mucoprotein moiety of gelatin may be separated for subsequent determination by partition in water - phenol (1:1). After the aq. phase has been treated with Dische's acid diphenylamine reagent (*cf.* Anderson and MacLagan, *Anal. Abstr.*, 1955, **2**, 2512), the extinction is determined spectrophotometrically at 530 mμ. The method is rapid and specific for mucoproteins and sialic acid. J. N. ASHLEY

3919. **Determination of protein in cerebrospinal fluid. Sources of error in the Lowry method.** H. A. Zondag and G. L. van Boetzelaer (St. Elisabeth's Hosp., Haarlem, The Netherlands). *Clin. Chim. Acta*, 1960, **5** (1), 155–156 (in English).—The Folin - Wu method is much more sensitive than the biuret method but is subject to serious errors caused by the presence of administered drugs (*e.g.*, salicylates) in the c.s.f. It is unreliable unless the extinction of the whole sample is corrected for the extinction given by the deproteinised fluid. The biuret method is not affected by the presence of such substances. H. F. W. KIRKPATRICK

3920. **Application of immuno-electrophoresis to biochemical and clinical problems.** G. Schwick (Behringwerke A.-G., Marburg/Lahn, Germany). *Chem. Weekbl.*, 1959, **55** (49), 701 (in German).—Some applications of immuno-electrophoresis to clinical problems are discussed, *e.g.*, in the diagnosis of dys- and para-proteinaemia, analysis of nephrosis sera, and determination of changes in protein composition. M. J. MAURICE

3921. **Spectrophotometric determination of nucleic acids.** R. G. Tsanev and G. G. Markov (Inst. Biochem., Bulg. Acad. Sci., Sofia). *Biokhimiya*, 1960, **25** (1), 151–159.—Nucleic acid fractions recovered from animal tissues usually contain impurities of a non-nucleotide nature which are the cause of falsely high values. A spectrophotometric method is proposed which gives accurate results even in the presence of such impurities if two appropriate wavelengths for measuring deoxyribonucleic acid (**I**) and ribonucleic acid (**II**) are used (extinction difference method). To establish these wavelengths, dry fixed tissue was extracted 6 times for 15 min. with *N* $HClO_4$ at 80°, the removal of nucleic acids being controlled spectrophotometrically. The nucleic acid-free protein residue was hydrolysed with *N* KOH in a boiling-water bath for 1 hr. The hydrolysate was pptd. with conc.

$HClO_4$ and the procedure, as described by Schmidt and Thannhauser (*J. Biol. Chem.*, 1945, **161**, 83) for alkaline hydrolysates containing nucleic acid, was followed. Finally an absorption curve was drawn. To determine nucleic acids, incubate dry fixed tissue with *N* KOH for 18 hr. at 37° (1 ml of *N* KOH per 100 mg of original tissue). Cool the hydrolysate, add conc. $HClO_4$ (0·1 ml per ml of *N* KOH) and separate the residue by centrifuging and washing with *N* $HClO_4$ in the cold. Combine the supernatant liquid containing **II** with the wash liquors and make up to a known vol. with *N* $HClO_4$. Extract **I** from the residue with *N* $HClO_4$ at 80° for 30 min. Use *N* KOH as a control for **I** and *N* $HClO_4$ for **II**. Measure the extinctions. Determine ribose by Mejbaum's method (*Hoppe-Seyl. Z.*, 1939, **258**, 117) with a 45-min. heating period and deoxyribose with diphenylamine by Dische's method (*Mikrochemie*, 1930, **8**, 4) with a 10-min. heating period. Determine P by the molybdenum blue method. With alkaline hydrolysates of 6 different normal and malignant tissues it is found from their absorption curves that the extinctions should be measured for **I** at 268 mμ and 284 mμ and for **II** at 260 mμ and 286 mμ. The amount of **I** is derived from the formula $800(E_{268} - E_{284})V/wl$ mg per 100 g of P, and the amount of **II** is derived from $561(E_{260} - E_{286})V/wl$ mg per 100 g of P, where E is the extinction of the extract at a particular wavelength, V the vol. of extract, *w* the wt. of the sample, and *l* the thickness of the layer. K. R. C.

3922. **Separation of ribonucleic acid nucleotides on ion-exchange paper.** R. M. Smillie (Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 557–558.—Chromatography is carried out by the ascending technique on cellulose paper impregnated with Amberlite XE-119 resin. Development is with 3·8 *N* formic acid and then, after cutting and drying the paper, with 0·5 *M* ammonium formate, pH 5·0. The position of the nucleotides is determined by pressing the developed chromatogram in contact with Whatman No. 1 paper impregnated with 0·1 *N* HCl. The "print" thus obtained is examined directly or by photography under u.v. light. W. H. C. Shaw

3923. **Colour reactions of steroids.** H. Wachsmuth and L. van Koeckhoven (Lab. Chim. et Biochim., Hôpital Stuivenberg, Antwerp, Belgium). *Anal. Chim. Acta*, 1960, **22** (1), 41–49 (in French).—Various selective reactions are described for the identification of steroids, and some of the reactions are adapted to quantitative spectrophotometric methods. A soln. of sodium molybdate in acetic acid yields a colour with free α-ketols. Sodium selenite gives a colour with Δ^5-steroids in the presence of phenol and $HClO_4$. Halphen's reaction (*cf. J. Pharm. Chim.*, 1902, **16**, 478) and the use of phthalaldehyde, tungsto-silicic and -phosphoric acids are also investigated. Quantitative methods are described for cortisone, methylandrostenediol, dehydro*epi*androsterone and oestrone.

H. N. S.

3924. **Determination of serum cholesterol with perchloric acid.** W. D. Brown (Kanematsu Memorial Inst. Path., Sydney Hospital, Australia). *Aust. J. Exp. Biol. Med. Sci.*, 1959, **37** (6), 523–531.—Serum cholesterol esters are hydrolysed by ethanolic KOH soln. and the free cholesterol is extracted with hexane. The evaporated extract is treated with acetyl chloride in dichloroethane containing a trace of $HClO_4$ and incubated at 50° for 15 min. The stable colour produced is measured at 523 mμ. Propionyl chloride may be substituted for acetyl chloride, in which case the colour is developed at 60° for 25 min. and the extinction is read at 526 mμ. The method is a modification of that of Trinder (*Analyst*, 1952, **77**, 321), but it is approx. 4 times as sensitive, and 8 times as sensitive as the Liebermann - Burchard procedure. Beer's law is obeyed if either the Beckman model DU or the Uvispek instrument is used, but not if the Hilger H810 absorptiometer is used. Micro- and ultra-micro methods (0·25 ml and 0·02 ml of serum) are described. The errors in the determination of cholesterol esters by oxidation methods are discussed.

E. C. Butterworth

3925. **Application of repeated development to the separation of steroids on paper.** M. Prusíková (Res. Inst. of Endocrin., Prague). *Experientia*, 1959, **15** (12), 460–461 (in German).—Chromatogram strips of Whatman No. 1 paper are dipped into a soln. of 30% formamide in methanol and then dried. Repeated development with different solvents permits the effective separation of certain steroids on one chromatogram. The method has been used to separate oestrogens. P. Nicholls

3926. **Rapid method for the estimation of urinary 17-oxosteroids.** F. Rappaport, J. Fischl and N. Pinto (Beilinson Hosp., Petach Tikva, Israel). *Clin. Chem.*, 1960, **6** (1), 16–22.—The method described is adapted from that of Drekter *et al.* (*J. Clin. Endocrin.*, 1947, **7**, 795) by using a small vol. of urine (5 ml) and extracting once with a larger vol. of ether (20 ml). Hydrolysis before extraction is carried out by adding conc. HCl (1·5 ml) and placing in a water bath at 80° to 85° for 12 min. The Zimmermann reaction is applied and the colour due to ketonic substances is isolated by $CHCl_3$ (3 ml) extraction. Turbidity in the $CHCl_3$ soln. is reduced by addition of polyethylene glycol (0·1 ml).

H. F. W. Kirkpatrick

3927. **An improved rapid method for free and conjugated 17-hydroxycorticosteroids in plasma.** L. Kornel (Birmingham Univ., Med. Dept., England). *J. Lab. Clin. Med.*, 1959, **54** (4), 659–668.—In the method described, free 17-hydroxycorticosteroids (**I**) are extracted from the heparinised sample (10 ml) with $CHCl_3$. *n*-Butanol is added to the $CHCl_3$ extract to stabilise **I**. After purification of the extract with solid Na_2CO_3 and centrifugation, half the $CHCl_3$ phase is extracted with a H_2SO_4 reagent (blank) and half with a phenylhydrazine - H_2SO_4 reagent for the colorimetric determination of free **I**. The aq. phase from the $CHCl_3$ extraction is treated with methanol to precipitate proteins, and CCl_4 is added. After centrifugation the extract is acidified and purified by extraction with hexane and a Ba acetate reagent. The purified conjugated **I** are then dissolved in a mixture of $CHCl_3$ and *n*-butanol and determined colorimetrically as described above. The coeff. of variation are, respectively, 2·3 and 5·9%. W. H. C. Shaw

3928. **Spectrophotometric analysis of multicomponent systems using the least-squares method in matrix form. The ergosterol irradiation system.** J. C. Sternberg, H. S. Stillo and R. H. Schwendeman (Kedzie Chem. Lab., Michigan State Univ., East Lansing, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 84–90.—The method described provides a rapid analysis of the five-component mixture obtained on irradiation of ergosterol, each component being determined

with a standard deviation of 4%. Better results are obtained when the matrix is based on extinction data at a large number of evenly spaced wavelengths, rather than on the wavelengths of max., min., and isosbestic absorbance.

K. A. PROCTOR

3929. **Modifications of two methods for the assay of amylase.** M. Somogyi (Jewish Hosp. of St. Louis, St. Louis, Mo., U.S.A.). *Clin. Chem.*, 1960, **6** (1), 23–35.—Modifications in the preparation of the substrates are described for the methods previously published by the author (*J. Biol. Chem.*, 1938, **125**, 399). H. F. W. KIRKPATRICK

3930. **Stable starch substrate for the determination of amylase in serum and other body fluids.** W. T. Caraway (McLaren Gen. Hosp., Flint, Mich., U.S.A.). *Amer. J. Clin. Path.*, 1959, **32** (1), 97–99.—The buffered starch substrate (pH 7·0) is stabilised by the addition of the equivalent of 1% of Na benzoate (Na_2HPO_4 13·3 g, benzoic acid 4·3 g, soluble starch 0·2 g, dissolved in water to 500 ml). Amylase action is followed by the starch - iodine reaction and the unhydrolysed starch is measured photometrically and compared with a control. This simple procedure takes 15 min. P. NICHOLLS

3931. **Paper-chromatographic method for lactase and maltase activity determination.** A. J. Philippu (Physiol. Lab., Univ. Athens, Greece). *Enzymologia*, 1960, **21** (4), 216–218 (in English).—The assay is carried out on tissue - substrate mixtures containing 4% by wt. either of lactose or of maltose, at respective pH values of 5·6 and 6·2. The proteins are pptd. with trichloroacetic acid and the enzyme activity is assayed in terms of residual substrate by a paper-chromatographic technique. The carbohydrates are separated by circular paper chromatography with the solvent system *n*-propanol - ethyl acetate - H_2O - α-picoline (14:2:4:9, by vol.). One half of the circle is sprayed to locate the positions, and the appropriate areas are cut out from the other half. The carbohydrate is then extracted with 5 ml of methanol at 70° for 20 min. The extract is transferred into 5 ml of methanol - H_3PO_4 - aniline (150:1:1, by vol.), and evaporated to dryness over a boiling-water bath. The residue is dissolved in 5 ml of methanol and the extinction of the soln. is measured at 400 mμ against a suitable blank. For standards, 50 to 500 μg of carbohydrate is used. S. BAAR

3932. **Studies on a new cellulase preparation from *Penicillium*. I. Method of determining enzymatic activity.** A. F. V. Eriksson and S. Lindvall (AB Astra, Res. Lab., Södertälje, Sweden). *J. Pharm. Pharmacol.*, 1959, **11** (12), 747–755.—Changes in the viscosity of an aq. soln. of Na carboxymethylcellulose in acetate buffer of pH 4·1 inoculated with the sample of cellulase are measured with an Ostwald viscometer at 37°. A mathematical treatment of the results is given which is suitable for the determination of enzymatic activity when the substrate is a polyelectrolyte or a polymer to which Staudinger's law is inapplicable. The ionic strength of a soln. of Na carboxymethylcellulose has a substantial effect upon the viscosity, and a cellulase preparation which contains salts must be purified before assay. A. R. ROGERS

3933. **Studies in histochemistry. LII. Quantitative determination of coenzyme A in microgram amounts of tissue by a microbiological technique.** R. M. Twedt, H. C. Lichstein and D. Glick (Minnesota Univ. Med. Sch., Minneapolis, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 374–381.—The two methods described are adaptations of that described by Novelli and Schmetz (*Brit. Abstr. C*, 1952, 517) and are suitable for the assay of microgram amounts of coenzyme A in tissue sections. The test organism is *Lactobacillus arabinosus* 17-5 (ATCC 8014), and the turbidity produced on its incubation in the presence of calcium pantothenate (standard) and hydrolysed coenzyme A is measured at 650 mμ. The macro-method requires the equivalent of up to 1·0 μg of calcium pantothenate in 10 ml and the micro-method 10 μl of a standard containing 10 to 100 mμg per ml. A method of assay for coenzyme A, without hydrolysis, is discussed. W. H. C. SHAW

3934. **The distribution of phospholipase B [and its determination] in mammalian tissues.** E. A. Marples and R. H. S. Thompson (Dept. of Clin. Path., Guy's Hosp. Med. Sch., London, England). *Biochem. J.*, 1960, **74** (1), 123–127.—Phospholipase B activity is estimated by the determination of the rate of release of free fatty acids and of glycerylphosphorylcholine when the homogenised tissues are incubated with lysolecithin. Both types of product are determined by standard methods and there is reasonable agreement between the two sets of results. J. N. ASHLEY

3935. **Colorimetric method for the assay of soluble succinic dehydrogenase and pyridine nucleotide-linked dehydrogenases.** H. A. Ells (Oklahoma Med. Res. Foundation, Oklahoma City, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 561–562.—The method for lactic and succinic dehydrogenases depends on the ability of phenazine methosulphate to induce electron transfer between reduced pyridine nucleotides and 2:6-dichlorophenolindophenol. The change in extinction at 600 mμ per min. is proportional to the enzyme concentration within the working range. W. H. C. SHAW

3936. **Biosynthesis of porphyrins from porphobilinogen by *Rhodospeudomonas spheroides*. II. Partial purification and some properties of porphobilinogen deaminase and uroporphyrinogen decarboxylase. [Determination of the decarboxylase.]** D. S. Hoare and H. Heath (Dept. of Chem. Path., Univ. Coll. Hosp. Med. Sch., London, England). *Biochem. J.*, 1959, **73** (4), 679–690.—The two enzymes are separated by pptn. with $(NH_4)_2SO_4$, and a reproducible indirect assay of the decarboxylase is described with porphobilinogen as the substrate and an excess of porphobilinogen deaminase. In the presence of the decarboxylase, coproporphyrin is formed and is determined spectrophotometrically by a standard method. J. N. ASHLEY

3937. **Cobalt activation of carboxypeptidase A. [Assay for the enzyme.]** J. E. Folk and J. A. Gladner (Nat. Inst. of Dental Res., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1960, **235** (1), 60–63.—A sensitive and convenient spectrophotometric method is described. It is similar to that described for the determination of acylase I by Mitz and Schlueter (*Anal. Abstr.*, 1958, **5**, 3488). Benzyloxycarbonyl-glycyl-L-alanine is used as the substrate and the extinction is measured at 232 or 233 mμ.

J. N. ASHLEY

3938. **Method for the determination of some amino-acid decarboxylases.** V. E. Davis and J. Awapara (Biol. Dept., Rice Inst., Houston, Tex., U.S.A.).

J. Biol. Chem., 1960, **235** (1), 124–127.—The amine formed by decarboxylation of the amino acid is separated from the amino acid by passage through a column of Amberlite CG-50 (H^+ form) and after being dissolved in 4 *N* acetic acid is determined spectrophotometrically at 279 mμ. The method is applicable to α-amino-acid decarboxylases but not to basic or dicarboxylic amino-acid decarboxylases. The main advantage is that the amine itself is measured and its presence can be demonstrated by paper chromatography. Fluorimetric methods or bioassays can be used for the determination of very low concn. of amine. J. N. ASHLEY

3939. **Assay, purification and properties of imidazole acetylase.** S. C. Kinsky (Washington Univ. Sch. of Med., St. Louis, Mo., U.S.A.). *J. Biol. Chem.*, 1960, **235** (1), 94–98.—The acetylase is assayed by a modification of the method of Brady and Stadtman (*J. Biol. Chem.*, 1954, **211**, 621) for the determination of thioltransacetylase by coupling the sequence of reactions: acetyl phosphate → acetyl coenzyme A; acetyl coenzyme A + imidazole → acetylimidazole; acetylimidazole + diethylaminoethanethiol → S-acetyldiethylaminoethanethiol. The first reaction is catalysed by phosphotransacetylase, and the non-enzymic transfer of acetyl in the third reaction is extremely rapid. The imidazole acetylase is measured by determining the effect of imidazole and enzyme on the production of thermostable hydroxamate-forming material. The thiol ester is determined by the hydroxamate method of Lipmann and Tuttle (*Brit. Abstr. C*, 1945, 276). J. N. ASHLEY

3940. **Streptococcal antihyaluronidase. I. Turbidimetric determination of hyaluronic acid.** M. Duval and A. German (Lab. Centr. de Biochim., Hôpital-Hospice de Bicêtre, Seine, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (12), 1613–1620.—The method is based on the turbidity produced when hyaluronic acid is added to a soln. of a quaternary ammonium salt, *e.g.*, benzalkonium chloride. The effects of pH, temp., concn. of benzalkonium chloride, ionic strength and time were studied. *Procedure*—The sample is added to 1% benzalkonium chloride soln. in an acetate buffer at pH 4·2 and after making up the soln. to a known vol. the extinction is measured after 30 min. in a 1-cm cell at 640 mμ. The plot of extinction *vs.* concn. is linear for 0 to 250 μg of hyaluronic acid.

II. Determination of streptococcal antihyaluronidase in serum. A. German, M. Duval and R. Leluc. *Ibid.*, 1959, **41** (12), 1621–1628.—Antihyaluronidase is assayed by determining its effect on hyaluronidase used to hydrolyse hyaluronic acid, which is determined turbidimetrically with benzalkonium chloride (*cf.* Duval and German, Part I, above). *Procedure*—Hyaluronidase is prepared by culture of a Group A Type 24 (A 4 NW) haemolytic streptococcus on a medium to which 0·2 g of hyaluronic acid per litre has been added. After 24 hr. at 37° the culture is filtered through a Chamberland candle and adjusted to pH 6·6 and lyophilised. It can be preserved in a refrigerator for one year. The hyaluronidase preparation is determined by the addition of standard hyaluronic acid followed by the measurement of the extinction at 640 mμ after 30 min. Spontaneous decomposition of the enzyme is minimised at 4°. For the determination of antihyaluronidase, the blood sample is taken without an anticoagulant (heparinised blood, in particular, should be avoided) and a series of dilutions of the serum from 1:500 in geometric progression are made. The diluted sera (0·5 ml) are added to 0·5 ml of phosphate buffer and 2 units of hyaluronidase are added (1 unit reduces the assay of hyaluronic acid from 200 μg to 100 μg in 30 min. at 37°). The tubes are left for 24 hr. at 4°, a soln. of hyaluronic acid is added (50 mg in 100 ml of phosphate buffer), the tubes are heated at 37° for 30 min. and 3 ml of benzalkonium chloride soln. (1% in acetate buffer) is added. After 30 min. the extinction due to the turbidity is read at 640 mμ. The vol. of serum neutralising 1 turbidimetric unit of hyaluronidase is calculated. A "healthy" blood does not contain > 3000 units per ml.

E. J. H. BIRCH

3941. **Assay, purification and properties of the adenylcobamide coenzyme.** H. A. Barker, R. D. Smyth, H. Weissbach, A. Munch-Petersen, J. I. Toohey, J. N. Ladd, B. E. Volcani and R. M. Wilson (Dept. of Agric. Biochem., Univ. of California, Berkeley, U.S.A.). *J. Biol. Chem.*, 1960, **235** (1), 181–190.—Two assay methods are described for the coenzyme form of pseudovitamin B_{12} (α-adenylcobamide). Both depend on the conversion of [^{14}C]glutamate into [^{14}C]mesaconate by an enzyme preparation from *Clostridium tetanomorphum* in the presence of the coenzyme. In the first method the reaction mixture is passed down a column of Dowex 50W (H^+ form), which retains the glutamate but not the mesaconate. The amount of ^{14}C in the percolate is a measure of the rate of the enzymic reaction under suitable conditions. The sensitivity of the method is determined by the specific activity of the [^{14}C]glutamate and the activity of the enzyme preparation. The method permits the detection of 1×10^{-4} μmole of coenzyme. The second method is more rapid and more accurate and is based on the spectrophotometric determination of mesaconate at 240 mμ. With low concn. of coenzyme the rate of change of extinction is practically linear with coenzyme concn. The assay does not determine other forms of cobamide vitamins. J. N. ASHLEY

See also Abstracts—**3600**, Fitting least-square lines to data. **3626**, Metals in biological materials. **3646**, **3647**, Zinc in org. material. **3793**, Hg in biological materials. **3971**, Antihistamines in animal organs. **4032**, Uric acid in poultry excreta. **4053**, Chromatographic measurements of amino acids. **4063**, **4064**, **4066**, **4068**, **4069**, **4071**, Electrophoresis of serum proteins. **4073**, Ashing of biological materials.

Pharmaceutical analysis

3942. **The use in drug analysis of the Schöniger combustion method for the determination of small amounts of phosphorus in organic substances, with a simplified colorimetric method for the determination of the same.** H. Kremsbrucker (Bundesanst. chem. u. pharm. Untersuchungen, Wien, Austria). *Sci. Pharm.*, 1959, **27** (4), 294–300.—Burn the sample in oxygen in a closed flask (*cf.* Schöniger, *Anal. Abstr.*, 1955, **2**, 1816) and absorb the products of combustion in H_2O. Acidify this soln. with 2 *N* H_2SO_4, add excess of aq. Br soln., boil, cool, and dilute with H_2O. Shake a 5-ml aliquot (containing 10 to 100 μg of P) with 10 *N* H_2SO_4 - H_2O - 8% aq. ammonium molybdate soln. (1:2:1) (4 ml) and *n*-butanol (5 ml) for 2 or 3 min., allow to separate, dry the organic phase with anhydrous Na_2SO_4 and measure the extinction at 426 mμ. Preliminary ashing is necessary for the determination of P-containing

drugs in pharmaceutical preparations. Interference by As can be overcome by a preliminary reduction to As^{III}, and Si does not interfere.
A. R. ROGERS

3943. **Determination of alkaloids by high-frequency titration.** F.-E. Raurich Sas and A. Tarrés Torras (Inst. "Alonso Barba," C.S.I.C., Barcelona). *Inf. Quím. Anal.*, 1960, **14** (1), 1–19.—After a review of the principles involved and the apparatus used in high-frequency titrimetry, details are given of the titration of alkaloid salts with 0·1 *N* NaOH by this method. Results on 10-mg samples of salts were within −3 to +2% of theroretical values.
G. H. FOXLEY

3944. **Identification of alkaloids and related compounds by paper chromatography and ultra-violet spectrophotometry.** R. Hilf, F. F. Castano and G. A. Lightbourn (U.S. Army Area Med. Lab., Fort Baker, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (4), 634–639.—Descending chromatography is carried out on Whatman No. 1 paper treated with buffers at pH 3·0, 5·0, 6·5 and 7·5 and then dried. Development is for 16 hr. with *n*-butanol equilibrated with the buffer. After drying, the papers are sprayed with an iodoplatinate reagent and the spots are cut out and eluted with 3 ml of 2% Na_2SO_3 soln. saturated with $NaBO_2$. The compounds are then extracted into $CHCl_3$ and back into 5 ml of 0·5 *N* HCl for u.v. spectrophotometry. R_F values of 15 alkaloids and antihistamines are listed.
W. H. C. SHAW

3945. **Micro-determination of alkaloids and alkaloid-like active substances in tablets, dragées and pills by means of Häussler's tropaeolin method.** W. Mohrschulz (Dtsch. Arzneiprüfungsinst., München). *Dtsch. ApothZtg.* 1960, **100** (2), 36–39.—The method of Häussler (*Anal. Abstr.*, 1958, **5**, 1662) has been applied to the determination of benactyzine in tablets, and of reserpine in dragées containing caffeine, salicylamide, Mg glutamate, 3:3-di-(*p*-acetoxyphenyl)oxindole and rauwolfia and yohimbe extracts.
A. G. COOPER

3946. **New titrimetric method for the determination of morphine.** S. Wolf (Phys.-Chem. Lab. der Firma Metrohm A.-G., Herisau, Switzerland). *Naturwissenschaften*, 1959, **46** (23), 649.—Dissolve the sample in *iso*propyl alcohol and titrate potentiometrically with 0·1 *N* KOH in *iso*propyl alcohol. Non-phenolic alkaloids, *e.g.*, codeine, do not interfere.
A. R. ROGERS

3947. **The control of injections and other pharmaceutical preparations by means of u.v. spectrophotometry as a standard analytical tool. V. Spectrophotometric assay of atropine sulphate injections.** H. J. van der Pol and R. F. Rekker (N. V. Kon. Pharm. Fabr. v/h Brocades-Stheeman & Pharmacia, Amsterdam-Meppel, The Netherlands). *Pharm. Weekbl.*, 1959, **94** (26), 845–852 (in English).—Atropine shows maximum absorption at 246, 251, 257 and 263 mμ. Since Beer's law is not obeyed, it is necessary to use different absorptivities for each concn. to be measured. The extinction of a 1% soln. measured in a 1-cm cell at 257 mμ is 5·57, 5·39 and 5·40 for concn. of 25, 50 and 100 mg per 100 ml, respectively. No preservative was present.
M. J. MAURICE

3948. **Analytical methods for rescinnamine.** S. R. Missan, L. L. Ciaccio, W. H. McMullen, H. J. Pazdera and T. C. Grenfell (Anal. Lab., Chas. Pfizer & Co., Inc., Brooklyn, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (1), 7–13.—Rescinnamine may be determined (*A*) by direct u.v. spectrophotometry at 308 mμ in $CHCl_3$, with correction for absorption due to reserpine; (*B*) by measurement of the fluorescence at 455 mμ in 3 *M* acetic acid excited by incident light of wavelength 310 mμ; (*C*) by oxidation with $NaNO_2$ and measurement of the fluorescence at 500 mμ with an activation wavelength of 385 mμ; or (*D*) by measurement of the decrease in u.v. absorption at 315 mμ on bromination in glacial acetic acid. Method *A* is preferred for bulk rescinnamine and method *C* for tablets. For crude rauwolfia preparations, the methods of choice are *A* and *D*. Method *B* is unreliable in the presence of traces of impurities, but is useful for a quick check of the purity of a sample.
A. R. ROGERS

3949. **Determination of the alkaloids of *Conium maculatum* by paper chromatography.** J. W. Fairbairn and P. N. Suwal, jun. (School of Pharmacy, Univ. of London). *Pharm. Acta Helv.*, 1959, **34** (12), 561–570 (in English).—Apply the sample mixture, at two "dose levels," and mixtures of known composition, also at two "dose levels," in 70% ethanol to the same sheet of Whatman No. 20 paper which has been washed with *N* HCl and with H_2O. Ensure that the four initial spot areas on the starting line are equal. Develop by the ascending technique with *tert.*-amyl alcohol - *tert.*-butyl alcohol - *N* HCl (9:3:2), dry in warm air, spray with bismuth iodide reagent (Munier and Macheboeuf, *Bull. Soc. Chim. Biol., Paris*, 1951, **33**, 846) and measure the spot areas. Calculate by the method of Fisher *et al.* (*Nature*, 1956, **164**, 183) with the assumption that the areas are directly proportional to the logarithms of the wt. of alkaloid. The results for coniine and γ-coniceine in an extract of *Conium* fruit agree well with those obtained spectrophotometrically (*cf.* Fairbairn and Challen, *Biochem. J.*, 1959, **72**, 556).
A. R. ROGERS

3950. **Comparative study of planimetric and densitometric methods in quantitative paper chromatography. Application to the determination of alkaloids and amines of broom (*Sarothamnus scoparius* L.).** F. Jaminet (Inst. Pharm., Univ., Liège, Belgium). *Pharm. Acta Helv.*, 1959, **34** (12), 571–584 (in French).—In the planimetric method, the relationship between spot area and quantity is logarithmic at low concn. and linear at higher concn. The results by the planimetric and densitometric methods are similar. The error of the mean of three determinations by either method is ≃ 3%.
A. R. ROGERS

3951. **Microchemical identification of some alkaloids, barbiturates, sulphonamides and new synthetic drugs. III.** T. P. A. van der Wegen (Farm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1959, **94** (22), 717–733.—For each of the following series of drugs a number of characteristic crystal reactions are given: harmaline, diamorphine, isoniazid, chiniofon, chlorpromazine, Larocaine, sulphamethizole, pipradrol, methadone, morphine, thiamine, nicotinamide and niketmhamide. (52 illustrations.)
M. J. MAURICE

3952. **Methods for the identification of some water-soluble derivatives of theophylline and theobromine, with special reference to paper chromatography.** H.

Kremsbrucker (Bundesanst. chem. u. pharm. Untersuchungen, Wien, Austria). *Sci. Pharm.*, 1959, **27** (4), 282–293.—Develop the sample on Whatman No. 1 paper with *n*-butanol - aq. NH_3 (*d*, 0·88) - H_2O (3:1:4) by the ascending technique for 16 hr. and identify the components by R_F values and by the colours and rates of colour formation with a modified Dragendorff reagent. The limit of detection is 60 μg for hydroxypropyltheophylline and dihydroxypropyltheophylline, and 20 μg for theobromine, theophylline, hydroxyethyltheophylline, hydroxypropyltheobromine and dihydroxypropyltheobromine. A. R. ROGERS

3953. **Improved spot reaction for cardiac glycosides.** K.-H. Segel (Dtsch. Akad. der Wissenschaften zu Berlin, Arbeitsstelle für Kreislaufforsch., Berlin, Germany). *Mikrochim. Acta*, 1960, (1), 27–30 (in German).—The reagent is 84% H_2SO_4 containing a small amount of 5% furfuraldehyde in $CHCl_3$. The colours obtained with **13** cardiac glycosides are tabulated. W. T. CARTER

3954. **Determination of gitoxin.** J. Lemli (Inst. de Pharmacog., Univ. Louvain, Belgium). *Pharm. Acta Helv.*, 1960, **35** (1–2), 36–42 (in French).—The reaction of Tattje (*Anal. Abstr.*, 1954, **1**, 2510) has been modified for the quant. determination of gitoxin in the presence of large amounts of digitoxin and organic impurities. *Procedure*—Hydrolyse the sample (0·5 to 2 mg) by heating on a boiling-water bath for 1 hr. with 35% ethanol (10 ml) and 4 *N* HCl (1 ml). Cool, extract with $CHCl_3$ (3 × 15 ml) and dilute the combined extracts to 50 ml. Evaporate to dryness an aliquot (containing 50 μg of gitoxin) and add the reagent [mix conc. H_2SO_4 (100 ml), 85% H_3PO_4 (100 ml) and 10% $Fe_2(SO_4)_3$ soln. (5 ml)] (10 ml) to the residue; set aside for 90 min. and measure the extinction at 572 mμ. Deduct a blank value obtained as follows—mix the residue from a second aliquot with 5 ml of reagent, set aside for 90 min., add methanol (5 ml) and measure the extinction after a further 10 min. A. R. ROGERS

3955. **Microbial assays of antibiotics using seeded plates stored in the refrigerator for several days to four weeks.** F. W. Bowman and S. Holdowsky (Food Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (12), 757–760.—The effect of storage at 5° on the zone of inhibition of penicillin (1 i.u. per ml) on assay plates seeded with *Staphylococcus aureus* (ATCC 6538 P) is studied. Plates with a light inoculum were satisfactory only on the day of preparation. With a heavy inoculum plates stored for 4 to 14 days were satisfactory, but older plates gave increased zones of inhibition; this effect could be counteracted by incubating the stored plates at 32° for several hours before use. W. H. C. SHAW

3956. **Assay method for the determination of penicillin in poliomyelitis vaccine.** V. A. Quinn (Wyeth Lab. Inc., West Chester, Pa., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (1), 17–19.—The vaccine sample (200 ml) is chilled, adjusted to pH 2·2 with 20% H_3PO_4, and extracted successively with 35, 15 and 15 ml of anhyd. diethyl ether. The ether extracts are combined and extracted three times with 2-ml quantities of cold 3% phosphate buffer, pH 7·0. The buffer extract is then assayed by a cup-plate method, with *Sarcina lutea* as test organism. Calibration (log concn. *vs.* zone diameter) is rectilinear with similarly extracted standards between 0·005 and 0·0002 unit per ml added to penicillin-free vaccine. W. H. C. SHAW

3957. **Polarographic studies on sarcomycin.** Keiji Ida (Meiji Seika Kaisha Ltd., Japan). *Bull. Agric. Chem. Soc. Japan*, 1960, **24** (1), 12–15 (in English).—The accurate polarographic assay of sarcomycin is only possible after suitable purification. Sarcomycin (25 to 500 mg) in aq. soln. is diluted to 20 ml with 0·1 *N* HCl (final pH < 2). The soln. is passed through a column (30 cm × 1·5 cm) of 20 ml of Duolite S-30 regenerated before use with 4% NaOH followed by 4% HCl. After adsorption, the column is rinsed with 0·01 *N* HCl and the sarcomycin is eluted with methanol. The first 5 to 10 ml of eluate is discarded and the further eluate is then collected up to the 50 ml mark in a volumetric flask containing citric acid soln. (21·014 g of citric acid and 11·69 g of NaCl dissolved in 1 litre of dil. HCl, final pH 2·0). The dissolved O is removed by bubbling H or N through the electrolytic cell. Polarography is carried out at −0·5 to −1·5 V. S. BAAR

3958. **Biological studies of streptimidone, a new antibiotic.** D. L. Kohberger, M. W. Fisher, M. M. Galbraith, A. B. Hillegas, P. E. Thompson and J. Ehrlich (Parke Davis & Co., Detroit, Mich., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (1), 9–16.—The details given include a paper-disc agar-diffusion method with *Kloeckera africana* (NRRL Y-1274) as test organism. Satisfactory inhibition zones are obtained with concn. of streptimidone between 70 and 2000 μg per ml. W. H. C. SHAW

3959. **Determination of vitamin B_{12} in the presence of intrinsic factor.** G. Machek and F. Lorenz (Kontroll-Lab. der Biochemie G.m.b.H., Kundl-Tirol). *Sci. Pharm.*, 1959, **27** (4), 209–215.—Extract the preparation (*e.g.*, tablets) with absolute ethanol, evaporate the extract to dryness, dissolve the residue in H_2O, filter, and determine vitamin B_{12} (**I**) in the filtrate, either spectrophotometrically at 361 mμ or microbiologically with *Escherichia coli*. For the spectrophotometric determination, 40 to 100 μg of **I** is used; the error is < 4%. For the microbiological method less **I** is used, but the results are less accurate. A. R. ROGERS

3960. **Determination of vitamin B_{12} in pharmaceutical vitamin preparations with *Escherichia coli*.** H. Janisch and H. Klaushofer (Lab. der Dr. A. Wander G.m.b.H., Wien, Austria). *Sci. Pharm.*, 1959, **27** (4), 222–227.—In the method described, *E. coli* ATCC 9637 (strain 113-3) is used in a simple liquid medium and agitation of the culture vessels is not necessary. Ascorbic acid does not interfere if NaCN has been added to the test soln. It is shown that intrinsic-factor concentrate contains a thermolabile water-soluble growth factor for *E. coli*. A. R. ROGERS

3961. **Estimation of resin in *Ipomoea hederacea* (Linn.) Jacq.** L. V. Kannan, P. C. Bose and G. K. Ray (Central Drug Res. Inst., Lucknow). *Indian J. Pharm.*, 1959, **21** (12), 341–342.—Remove fat from the powdered seeds (60 mesh) (5 g) by continuous extraction with light petroleum (boiling-range 40° to 60°). Dry the residue at 40° and heat under reflux for 4 hr. with methanol (50 ml). Percolate with warm methanol and dilute the combined soln. to 100 ml with methanol. Mix a 20-ml aliquot with $CHCl_3$ (10 ml) and shake with 1% aq. HCl (10 ml). Wash the aq. layer with methanol -

$CHCl_3$ (1:2) (3 × 15 ml) and add the washings to the organic layer. Shake again with 1% HCl and wash as before. Treat the combined extracts with anhydrous Na_2SO_4, filter, evaporate to dryness and weigh the residue. A. R. ROGERS

3962. **Spectrophotometric method of determining some anthracene derivatives in frangula bark (*Rhamnus frangula* L.).** B. Lipiński (Pharm. Inst., Warsaw). *Acta Polon. Pharm.*, 1959, **16** (6), 467–473.—*Procedure*—Weigh 0·1 g of the bark, add 5 ml of 25% HCl and 25 ml of 95% ethanol and heat on a water bath for 80 min. Cool, filter into a 500-ml separating-funnel, wash the flask with 5 ml of ethanol and filter the washings into the main soln. Add 50 ml of benzene and shake for 5 min. Add water (300 ml), shake and set aside for 2 hr. Discard the aq. ethanol layer, filter the benzene layer through a filter-paper containing ≃ 5 g of anhyd. Na_2SO_4 into a 50-ml flask and make up to vol. with benzene. Take a suitable aliquot, dilute with benzene as required (usually 1:4000) and measure the extinction against benzene in a Beckman spectrophotometer at 360 mμ and 430 mμ, and calculate the amount of reduced and oxidised anthracene derivatives as 1:8-dihydroxyanthranol and 1:8-dihydroxyanthraquinone, respectively, these compounds being used as standards. W. ROUBO

3963. **Adsorption chromatographic separation of barbiturates.** M. Sahli and M. Huber (Lab. der Interkanton. Kontrollstelle für Heilmittel, Bern, Switzerland). *Sci. Pharm.*, 1959, **27** (4), 271–276.—To separate Bromadal (carbromal) (**I**) and phenobarbitone (**II**) (100 mg of each), apply the mixture to a column of aluminium oxide (10 g) - H_2O (1 ml), elute **I** with benzene - diethyl ether (97:3) (70 ml) and then elute **II** with benzene - diethyl ether (1:1) (10 ml) followed by diethyl ether (30 ml); separation is complete. Semi-quantitative separation of aprobarbital and barbitone, and of methylphenobarbitone and phenytoin is possible with similar columns and solvents. A. R. ROGERS

3964. **Determination of diphenylhydantoin [phenytoin] in tablets.** F. Biedebach and G. Manns (Inst. Landesapothekerkammer Hessen, Frankfurt/M.). *Arch. Pharm., Berlin*, 1960, **293** (1); *Mitt. dtsch. pharm. Ges.*, 1960, **30** (1), 1–6.—The method is based on the reaction of phenytoin (**I**) with ammonium carbonate and $CuSO_4.(NH_4)_2SO_4$ to form an insoluble complex $(C_{15}H_{11}O_2N_2)_2Cu + 4[(C_{15}H_{11}O_2N_2)_2Cu(NH_3)_2]$. Weigh accurately ≃ 0·25 g of the powdered tablets, extract with boiling acetone (40 ml) for 15 min., filter and repeat the extraction with acetone (2 × 20 ml). Evaporate the extract, dissolve the residue in *N* NaOH (2 ml) and H_2O (1·5 ml), and add freshly prepared 5% ammonium carbonate soln. (2 ml) and 5% $CuSO_4.(NH_4)_2SO_4$ soln. (2·5 ml). Filter after 2 hr., wash the ppt. with water (30 ml) and dry to constant wt. at 40°. The factor for **I** is 0·85. Numerous barbiturates, caffeine, phenazone, stearic acid, Na lauryl sulphate, Tween 60, etc., did not interfere. A. G. COOPER

3965. **Ion exchange and spectrophotometry in organic pharmaceutical analysis. II. Simultaneous determination of pyrazolones and alkaloid bases.** E. Häberli and E. Béguin (Anal. Lab. der Siegfried A.-G., Zofingen, Switzerland). *Pharm. Acta Helv.*, 1960, **35** (1–2), 13–21 (in German).—The separation of amidopyrine (**I**) or phenazone (**II**) from quinine (**III**), codeine, papaverine or yohimbine is described. The bases are adsorbed on to Dowex 50-X2; **I** and **II** are eluted with borate buffer soln. (pH 7·6) and the alkaloids with methanolic NH_3 (700 ml of methanol mixed with 300 ml of 25% aq. NH_3) and the separated compounds are determined by u.v. spectrophotometry at a suitable wavelength. The errors are < 1%. The method has been extended to the quant. determination of all components of a mixture of **I**, **II**, **III**, salicylic acid, caffeine and phenacetin (*cf. Anal. Abstr.*, 1959, **6**, 4128). A. R. ROGERS

3966. **Qualitative identification of local anaesthetics in their dosage forms.** H. M. Koehler and E. G. Feldmann (Div. of Chem., American Dental Ass., Chicago, Ill.). *Anal. Chem.*, 1960, **32** (1), 28–31.—The recommended procedures are descending paper chromatography with either butyl alcohol - 37·5% aq. HCl - H_2O (12:2:15) or butyl alcohol - glacial acetic acid - H_2O (4:1:5) as solvent system and detection in u.v. light or by a modified Dragendorff reagent or $KMnO_4$ spray; formation of picrate; formation of tetraphenylborate; measurement of u.v. absorption spectrum. Data are given for 16 local anaesthetics. A. R. ROGERS

3967. **Influence of some amino acids on the electrophoretic behaviour of local anaesthetics.** G. Marras and E. Farina (Ist. Farmacol. e Chim. Generale, Univ. Sassari, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1960, **36** (2), 53–55.—The effect of various amino acids on the electrophoretic migration of the local anaesthetic Farmocaina (2-diethylaminoethyl *p*-butylaminobenzoate hydrochloride), lignocaine, amylocaine and cinchocaine was studied on Whatman 3 MM paper (40 mm × 400 mm) in a buffer at pH 2·1, with an electric field of 7 V per cm applied for 3 hr. In all cases the molecular ratio of anaesthetic to amino acid was 1 to 4, and zones were detected with Dragendorff reagent and with ninhydrin, respectively. Aspartic acid, tryptophan, cysteine and leucine all reduced the rate of migration of the local anaesthetics, while the other amino acids tested were without effect except on amylocaine. The migration of the amino acids was unaffected by the presence of the anaesthetics. The amino acids (except cysteine) were detected in the eluate from the retarded zone of local anaesthetic, and it is probable that the *in vivo* action of these amino acids in annulling surface anaesthetic activity may be ascribed to the formation of chemical or physico-chemical complexes. E. C. APLING

3968. **Note on the determination of nikethamide.** B. Baehler and J. Rabinowitz (Lab. de l'École de Chim., Genève). *Pharm. Acta Helv.*, 1960, **35** (1–2), 22–23 (in French).—Dissolve the sample (250 mg) in water (10 ml) and add a 50% (w/w) soln. of KOH (10 ml). Steam-distil in a Kjeldahl apparatus into 4% aq. H_3BO_3 soln. (10 ml) during 45 min. and titrate with 0·1 *N* HCl with bromocresol green - methyl red as indicator. A relative precision of 1 to 2% is claimed. A. R. ROGERS

3969. **Determination of isoniazid and N-acetyl-D-glucosaminyl *iso*nicotinic acid hydrazide with sodium 1:2-naphthaquinone-4-sulphonate.** W. Nielsch and L. Giefer (Anal. Lab., J. A. Benckiser G.m.b.H., Ludwigshafen, Rhein, Germany). *Mikrochim. Acta*, 1960, (1), 17–26 (in German).—The reagent gives a coloured complex with isoniazid (**I**) at pH 8·5. The extinction is measured at 440 to 480 mμ after bleaching the excess of reagent with

Na_2SO_3. N-Acetyl-D-glucosaminyl *iso*nicotinic acid hydrazide does not react unless it is hydrolysed by heating the neutral soln. under reflux for 2 hr. before the test. Many metabolites of **I** and numerous other substances give positive reactions, and positive results have been obtained on samples of serum and urine known to contain no **I**. It is concluded that the method is not applicable to samples of biological origin. W. T. CARTER

3970. **Colorimetric determination of dextrosulphenidol and raceophenidol.** E. W. McChesney, J. M. Shekosky, H. W. Eckert and R. F. Koss (Sterling-Winthrop Res. Inst., Rensselaer, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (1), 28–32.—The method involves hydrolysis of the compound being determined in hot 0·1 *N* NaOH and oxidation by periodate to *p*-methylsulphonylbenzaldehyde, which is extracted by $CHCl_3$ and determined colorimetrically at 570 mμ as the alkali salt of its *p*-nitrophenylhydrazone in methanolic soln. Preliminary preparation of samples of urine, serum, tissue, faeces, eggs or poultry feed may involve homogenisation with H_2O, partition between ethyl acetate and H_2O to remove H_2O-soluble extractives, and partition between aq. methanol and hexane. The recovery ranges from 70 to 100%. Blanks and standard samples should be determined.
A. R. ROGERS

3971. **Identification of antihistamines in post-mortem organs.** G. Machata (Inst. Forensic Med., Univ. Vienna). *Arch. Toxikol.*, 1960, **18**, 124–130.—Details for the quant. analysis of tissue and blood for phenothiazines are described. The acidified tissue homogenate is extracted with cold ethanol. The alcoholic extract is concentrated *in vacuo*. The dry residue is de-fatted with NaCl at moderate heat, concentrated, stirred into absolute ethanol, suction-filtered and again concentrated by distillation. The residue is completely soluble in H_2O. It is extracted with ether and $CHCl_3$ and then made alkaline with aq. NH_3. This precipitates the base which can be extracted with $CHCl_3$. The extract is filtered and evaporated. For the spectrophotometric determination it is dissolved in a suitable amount of absolute ethanol. The absorption max. of mepyramine base is at 312 mμ. As little as 10 μg of the base can be measured. S. BAAR

3972. **Complexometry in organic analysis. VII. Determination of organic bases with cadmium complexonate.** B. Buděšínský and J. Körbl (Res. Inst. Pharm. Biochem., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (1), 76–85.—On the basis of the study of the system EDTA (cadmium salt) - iodide, the solubility products of complexes of CdI_2 with several organic bases were determined and a method for the semi-micro determination of gallamine triethiodide, chlorpromazine, quinine and piperidinium bromide was worked out. The described method is based on the titration of the EDTA (disodium salt) (**I**) set free with a Ca salt, with methylthymol blue as indicator, after the separation of the difficultly soluble CdI_2 complexes. These compounds can also be determined in the presence of some bases (*e.g.*, quinine in the presence of amidopyrine) if certain conditions are maintained. *Procedure*—Dissolve the sample (30 mg) in 0·25 *N* H_2SO_4 (15 ml), add the reagent (5 ml), mix, and filter after 5 min. Reject the first 3 ml of the filtrate; to another 10 ml add twice-distilled H_2O (30 ml), aq. NH_3 (25%) (10 ml) and methylthymol blue as indicator, and titrate with 0·01 *M* $CaCl_2$ till the colour turns violet. To prepare the reagent dissolve 93 g of **I** in 400 ml of H_2O, and add 70 g of cryst. $CdSO_4$; after 5 min. make alkaline with 34 g of anhyd. Na_2CO_3 to pH 8 or 9; after 12 hr. filter, dilute to 670 ml with H_2O, add 830 g of KI, shake for 1 hr. and filter. J. ZÝKA

3973. **Chromatography of aromatic isomers. XIII. Determination of toluenesulphonamides and *p*-sulphamoylbenzoic acid in saccharin.** J. Franc (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (12), 3881–3886 (in German).—After nitration the products formed are determined chromatographically and polarographically. The relation between the dipole moment and R_F value was used for the identification of some amides after nitration. The course of the nitration and oxidation of some derivatives was studied. The nitration of technical saccharin (**I**) was carried out for 15 min., at 0°, with a mixture of conc. H_2SO_4 and HNO_3 (2:1) (2 ml) and the product was diluted with H_2O (5 ml) and pyridine (3 ml). The chromatographic separation was carried out on Whatman paper No. 4 with *n*-butanol - pyridine - H_2O (1:1:1) as solvent. The separated spots were detected with Ehrlich reagent after reduction with $SnCl_2$ soln. A new direct polarographic method for the determination of the purity of **I** was developed. For this, the nitrated sample was diluted with H_2O (5 ml) and with Britton - Robinson buffer soln. (pH 1·8) (diluted 1:1 with H_2O) to 50 ml, and the polarogram recorded. J. ZÝKA

3974. **Determination of saccharin.** P. M. Parikh and S. P. Mukherji (Zandu Pharm. Works Ltd., Bombay, India). *Analyst*, 1960, **85**, 25–26.—Saccharin is dissolved in water containing dil. aq. NH_3; sodium saccharin and elixir of saccharin are dissolved in water. The soln. is acidified with acetic acid, 0·1 *N* $AgNO_3$ is added, the mixture is heated in boiling water, then cooled in an ice bath, and the ppt. is separated by suction through a ground glass filter and washed with ice-cold water. The filtrate is acidified with HNO_3, $(NH_4)_2SO_4$·$Fe_2(SO_4)_3$ indicator is added, and the residual $AgNO_3$ is determined by titration with 0·1 *N* NH_4SCN. The determination is corrected for a reagent blank. Saccharin tablets are shaken with a known vol. of water, the liquid is filtered, the first portion of the filtrate is rejected and an aliquot of the remainder is treated as before. If the tablets contain $NaHCO_3$, sufficient acetic acid must be added to ensure a pH below 6. If Cl^- are present, the silver - saccharin ppt. is extracted on the filter with warm dil. HNO_3 and the combined Ag is determined in the extract. Sodium cyclamate does not interfere. A. O. JONES

3975. **Determination of the "bleeding number" of petrolatum.** H. J. van der Pol (Control Lab. N.V. Kon. Pharm. Fabr. v/h Brocades, Stheeman en Pharmacia, Meppel, Netherlands). *Pharm. Weekbl.*, 1960, **95** (1), 3–8 (in English).—Results obtained by the method of Kinsel and Phillips (*Petrol. Ref.*, 1948, **27**, 428) proved to be dependent on the operator. The bleeding number is influenced by a number of factors, which must be rigorously standardised. *Procedure*—Melt a 200-g sample and allow it to cool to about 10° above its melting-point, stir with a rod, pour into an ointment tin (4 cm diam. × 3·5 cm depth) until it is completely filled and store for at least 4 hr. at room temp. Immerse

exactly 2 cm (previously marked with pencil) of a strip of filter-paper (S. & S. 2043b mgl, 15 cm × 2 cm, cut in the machine direction) perpendicularly in the sample, and place in an incubator for 24 hr. at 37°. Withdraw the strip, remove the adhering petrolatum and measure the height of ascent from the 2-cm mark. This height, in mm, gives the bleeding number. In the case of a slightly curved boundary, measure the height to the lowest point. Carry out the test in triplicate and report the bleeding number as the average of at least two determinations that do not differ by more than 5% of the mean value. The standard deviation is ±2·1 for a bleeding number of 68.

M. J. MAURICE

3976. **Thin-layer chromatography in toxicology.** G. Machata (Inst. für gerichtl. Med., Univ. Wien, Austria). *Mikrochim. Acta*, 1960, (1), 79–86 (in German).—A chromatographic technique is described in which sheets of glass coated with a thin layer of silica gel bonded with gypsum are used (*cf.* Stahl, *Pharmazie*, 1956, **11**, 633). The advantages over paper chromatography are that the development time is only 1 hr., several milligrams of material can be separated, and simple solvents are used. Examples of the separation of barbiturates and alkaloids and a list of spray reagents are given.

W. T. CARTER

3977. **The determination, in forensic toxicology, of metallic poisons by paper chromatography.** Dharam Narain Tripathi and Swarup Narain Tewari (Clin. Lab. 18/3A, The Mall, Kanpur, India). *Z. anal. Chem.*, 1960, **172** (3), 161–162 (in English).—Nine metals likely to be present in internal organs as a result of poisoning can be detected by the use of two chromatograms. Since the tests are conducted on an HCl soln. of the ashed sample they are capable of wide application. One drop of the soln. is placed at the centre of a No. 1 Whatman filter-paper and is developed with *n*-butanol saturated with *N* HCl. After the paper has been dried it is sprayed with a soln. of diphenylcarbazide, when coloured bands are formed with Pb (grey, R_F 0·00), Cu (green, R_F 0·10), Bi (orange, R_F 0·63), Zn (red, R_F 0·71) and Hg (greyish red, R_F 0·96). Another drop is placed on a second paper and developed with a mixture of acetylacetone saturated with water to which has been added 0·5% of HCl and 25% of acetone. The dried paper is sprayed with a soln. of dithizone in $CHCl_3$; Sb gives a band with R_F 0·53, and As a band with R_F 0·18; by spraying with rhodizonic acid, Ba (R_F 0·45) can be detected. H. M.

3978. **Use of pepsin in the toxicological analysis of food products. Digestion of the material and detection of some heavy metals.** J. Piechocka and M. Nikonorow (Dept. of Food Res., State Inst. of Hygiene, Warsaw). *Acta Polon. Pharm.*, 1959, **16** (6), 437–444.—The feasibility of using pepsin for the digestion of protein material instead of mineralising according to the Fresenius - Babo method has been examined. Chlorides of As, Pb, Th, Cu, Hg and Zn were used and the influence exerted by these metals individually, or in admixture, upon the digestive activity of pepsin was studied. Both qual. and quant. analyses have been carried out and it is shown that digestion by pepsin can be used for the isolation, detection and quant. determination of the metals named. The procedure takes one-quarter of the time for the mineralisation method and opens up further possibilities in toxicological analysis. W. ROUBO

See also Abstracts—**3809**, Titration of caffeine and phenazone. **3845**, Quaternary ammonium compounds. **3872**, Cobalt in vitamin prep. **3873**, Glutethimide in biol. fluids. **3874**, Phenothiazine compounds in urine. **3875**, Identification of sulphadiazine. **3879**, Separation of deoxy sugars. **3885**, **3886**, Separation of vitamin B_{12}. **3893**, Determination of adrenaline and noradrenaline. **3992**, Hexamine in foods.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

3979. **Determination of moisture content in cereals. I. Interaction of type of cereal and oven method.** T. A. Oxley, S. W. Pixton and R. W. Howe (Pest Infestation Lab., London Rd., Slough, England). *J. Sci. Food Agric.*, 1960, **11** (1), 18–25.—Moisture content values obtained by five different oven-drying methods are compared for a number of coarsely ground cereal grains, for wheat-gluten, and for pure wheat, maize and rice starches at different moisture levels. The differences between methods vary with the type of grain, and are less for high-protein hard wheats, parboiled rice and flint maize than for soft wheats, milled rice, dent maize, oats or barley. The maximum range of moisture content found for one sample was 0·62%. E. C. APLING

3980. **Detection and estimation of fungal amylases in flour.** R. A. Knight (Baking Ind. Res. Sta., Chorleywood, Herts., England). *J. Sci. Food Agric.*, 1960, **11** (1), 54–60.—The method depends on the measurement of the loss of α-amylase activity that occurs when a flour extract containing Ca^{2+} is heated at 68° for 30 min. Under these conditions the loss of fungal α-amylase is 83% (±5%) and of cereal α-amylase ≃ 10%. Assuming average losses on heating, the relative proportions of fungal and cereal α-amylase are calculated from determinations of α-amylase activity in heated and unheated portions of flour extract, by using the method of Jongh (*cf. Chem. Weekbl.*, 1957, **53**, 597). Confirmation of the amount of fungal amylase addition is provided by the relationship between Hagberg no. (x) and cereal α-amylase activity (y), given by the equation, $y = -0·196 + 0·028x$. E. C. APLING

3981. **Determination of uric acid in wheat flour infested by *Tribolium castaneum*, by using paper chromatography.** S. Venkatrao, K. Krishnamurthy, M. Swaminathan and V. Subrahmanyan. *Cereal Chem.*, 1960, **37** (1), 93–96.—Uric acid was determined in control and infested samples of wheat flour by a colorimetric method and by paper chromatography, with the descending technique and *n*-butanol - acetic acid - water (4 : 1 : 5) as the developing solvent. Tungstoarsenophosphoric acid was the spray reagent. The colorimetric and chromatographic methods of assay are compared and discussed. J. V. RUSSO

3982. **The formation, constitution and determination of aroma-producing substances in bread.** M. Rothe and B. Thomas (Inst. f. Ernährung Potsdam-Rehbrücke, Deutsch. Akad. Wissenschaften, Berlin).

Nahrung, 1959, **3** (1), 1–17.—The compounds which contribute mainly to the aroma of bread are aldehydes, and particularly amino-acid aldehydes. The formation of these aldehydes during rising, and the mechanism of the reactions they undergo during the baking process, are discussed. A method for the determination of volatile aldehydes in bread, formed during non-enzymic browning reactions, has been developed and different types of bread have been examined. Results are tabulated and discussed. The taste values were found to be related to the aldehyde content; with increased baking time the aldehyde content rises. Diffusion of volatile aldehydes from crust to crumb during storage has been observed; on longer storage a parallel destruction of crumb aldehydes takes place. S. M. MARSH

3983. **Dextrose and maltose contents of commercial liquid glucose.** S. J. Patterson and J. L. Buchan (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 75–76.—The proportions of individual sugars in liquid glucose often affect the texture and storage life of confectionery and other food products, and the more conventional data, *viz*, Baumé and "dextrose equivalent," used by manufacturers do not indicate the precise content of individual sugars. It has been shown by paper chromatography that classical methods of analysis give high results for maltose. The maltose and dextrose contents of a number of samples of liquid glucose were determined by Patterson and Savage's carbon-column method (*Ibid.*, 1957, **82**, 812) and are quoted together with the conventional data supplied by the manufacturers. A. O. JONES

3984. **Rapid method for the determination of sugar in potatoes for the correction of the calculation of yields in potato-starch manufacture.** W. Maurer and E. Blaško (Zentrallab. f. Stärkeindustrie, Kyritz). *Nahrung*, 1959, **3** (1), 55–75.—Methods for the determination of starch and sugar in potatoes are reviewed. Preliminary experiments on the absorption of salts, albumin and amino acids from potato juice by treatment with Wofatit anion-exchange resins and neutral Wofatit mixtures are described. A rapid method for the determination of sugar has been developed in which juice is centrifuged to remove solids, treated with a specially prepared resin and the sugar content of the residual liquor is then measured refractometrically or interferometrically. The method of calculation is described. The relative deviation of the results as compared with other chemical methods is $\pm 5\%$ with a maximum of 10%. A slightly more elaborate standard method based on the above procedure is also described. S. M. MARSH

3985. **Determination of gum acacia in confectionery products.** P. Fostier. *Ann. Falsif.*, 1960, **53**, 18–23.—The method proposed involves hydrolysis with dilute HCl with subsequent degradation of the sugars formed to give furfuraldehyde. This is determined by collecting it as a distillate and precipitating with a solution of phloroglucinol (11 g of phloroglucinol in 1500 ml of 12% HCl). The ppt. is filtered off, dried and weighed, and a formula is used to give the amount of gum present from the weight thus determined. The method is not applicable if gums other than gum acacia are present. S. M. MARSH

3986. **Detection of rennet in "entremets."** J. Pien, B. Lefebvre and A. Frêne. *Ann. Falsif.*, 1960, **53**, 9–17.—A method is described for the detection and estimation of rennet in so-called "fermented milk" products. Whey is separated from the sample by centrifuging and is titrated to determine the acidity (usually $\geq$ 1 to 2 g per litre, expressed as lactic acid) in order to ensure the presence of a compound unaltered by fermentation. The whey is then evaporated under reduced pressure at a max. temp. of 40° to give a final vol. of 1 to 2 ml. Pasteurised skimmed milk, containing 1 g of $CaCl_2$ and 2 ml of commercial (30%) formalin per litre, is then added to give a vol. equal to that of the whey originally extracted, and the mixture is left to stand at 37°. The coagulation time is noted. The actual amount of rennet present can be estimated by comparing the coagulation time with those for mixtures containing known amounts of rennet obtained under similar conditions. The method will detect amounts of rennet to a lower limit of 0·003% of rennet of 1:10,000 strength in the whey. S. M. MARSH

3987. **The importance and detection of antibiotics in milk.** W. Wodsak (Chem.-u. Lebensmitteluntersuchungsanst. d. Hygien. Inst., Hamburg, Germany). *Nahrung*, 1959, **3** (7–8), 729–736.—The presence of antibiotics in milk leads to difficulties in processing and may have harmful effects on the consumer. Because of the small amounts usually present in milk, a combination of microbiological and chemical methods is most promising for the detection of antibiotics. Several such procedures are described and discussed. S. M. MARSH

3988. **Distillation method for the quantitative determination of malonaldehyde in rancid foods.** B. G. Tarladgis, B. M. Watts, M. T. Younathan and L. Dugan, jun. (Florida State Univ., Tallahassee). *J. Amer. Oil Chem. Soc.*, 1960, **37** (1), 44–48.—A simplified Sidwell distillation technique is described for meat and compared with the extraction method of Turner *et al.* (*Food Technol.*, 1954, **8**, 326). A 10% aqueous meat slurry (adjusted to pH 1·5 with HCl) is boiled in a Kjeldahl flask until half the water has distilled. Aliquots treated with 0·02 *M* thiobarbituric acid (**I**) in 90% glacial acetic acid are then compared spectrophotometrically with standard curves of 0·001 *M* aq. 1:1:3:3-tetraethoxypropane (**II**). The effect of varying pH, heating time and amount of recovered distillate was examined in relation to the **II** standard. Results suggest that less fat oxidation occurs during the test itself than with other techniques. High correlation of **I** numbers with rancid odour is also established, although malonaldehyde only plays a small part in the basic odour. P. M. KINGSTON

3989. **Quantitative oscillographic determination of vanillin and bourbonal [3-ethoxy-4-hydroxybenzaldehyde] in vanilla-sugar, and in pudding- and sauce-mixes.** H. Woggon and K. Rauscher (Inst. f. Ernährung, Potsdam-Rehbrücke, Deutschen Akad. Wissenschaften, Berlin, Germany). *Nahrung*, 1959, **3** (2), 161–173.—Methods available for the determination of vanillin are briefly reviewed. Details of an oscillographic procedure are given, with a circuit diagram, in which semicarbazide hydrochloride (0·5 *M*, 0·1 *N* in HCl) is used as electrolyte. The vanillin or bourbonal concn. (0·5 to 6 $\times$ 10^{-4} molar) is determined by measurement of the depth of the cut-in on the oscillogram, and reference to a calibration curve. Typical results are tabulated and discussed. The method is suitable for qualitative

control, the main advantage being that no preliminary treatment of the sample is necessary, since other substances present therein do not interfere.
S. M. MARSH

3990. **The quantitative determination of 15 food colours.** B. Koether (Chem. Untersuch. f. Saarland, Saarbrücken). *Dtsch. LebensmittRdsch.*, 1960, **56** (1), 7–13.—The amount of pure dyestuff used in transparent foodstuffs is from 0·5 mg per 100 g for yellow colours to 2·5 mg per 100 g for red, and in opaque foods, about 5 mg per 100 g. The 15 simple food colours, and most binary mixtures, can be quant. determined photometrically with sufficient accuracy by measuring the extinction at the selected wavelengths of 405, 578 and 644 mμ. The specific extinction of the 15 colours are reported for various pH values, and pH 4·25 is chosen for quant. measurements. The isolation of colours from food by the classical wool separation is not quant., and two of the colours are irreversibly changed. The colours can be isolated from their soln. in 70% ethanol by adsorption on acid alumina, a mixture of acid and basic alumina, or a strongly basic ion-exchange resin. Elution from alumina with pH 4·25 buffer is quant., but recovery from the resin varies from 50 to 80%. E. C. APLING

3991. **Determination of sulphurous acid in foodstuffs, especially dehydrated vegetables.** H. Zonneveld and A. Meyer (Inst. f. Aufbewahrung und Verwertung von Gartenbauerzeugnissen, Wageningen, Netherlands). *Z. LebensmittUntersuch.*, 1960, **111** (3), 198–207.—Four established methods for the determination of SO_2 are compared. These methods were found to be unsuitable for dehydrated cabbage, onions and leeks, because these vegetables contain interfering compounds. A modified Monier-Williams method has been developed which gives accurate results. The sample is weighed into an SO_2-free gelatin capsule and introduced into a flask containing 225 ml of methanol, 50 ml of H_2O and 50 ml of 4 *N* HCl which has been brought to the boil and through which passes N at the rate of 30 to 35 bubbles per min. Boiling is continued for 1 hr. The distillate is received in 12·5 ml of H_2O_2 and bromophenol blue as indicator. After washing the condenser, etc., the distillate and washings are made up to ≃ 75 ml and titrated from a microburette with 0·1 *N* NaOH. (Apparatus illustrated.)
I. DICKINSON

3992. **Determination of hexamine [in foods].** W. Diemair and A. Heiligenthal (Inst. f. Lebensmitt-Chemie, Frankfurt-am-Main). *Z. LebensmittUntersuch.*, 1960, **111** (3), 208–214.—The preservative value of hexamine lies in the fact that it splits up in an acid medium into formaldehyde and ammonia. A colorimetric method is given in which phloroglucinol - NaOH is used for the determination of formaldehyde in the presence of hexamine.
I. DICKINSON

3993. **Determination of hexachlorocyclohexane residues in foodstuffs.** R. Wood (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 21–24.—A hexane extract of the sample is treated with a mixture of conc. and fuming H_2SO_4 and after separation is passed through a Celite - H_2SO_4 column. The residue obtained by evaporation of the percolate at low temp. is boiled under reflux with malonic acid and glacial acetic acid, and the cooled liquid is treated with more malonic acid, zinc dust and glacial acetic acid. The liquid is heated in the dechlorination apparatus of Hancock and Laws (*Analyst*, 1955, **80**, 665), with a sintered-glass bubbler (described) immersed in a nitration mixture. The nitration product (*m*-dinitrobenzene) is extracted with dichloromethane, the extract is washed with alkali, dried and evaporated, and the residue is dissolved in ethyl methyl ketone. An aliquot is shaken mechanically with 50% KOH soln. and, after development of the colour, the extinction is measured and referred to a calibration graph. Recovery of known amounts of hexachlorocyclohexane added to various vegetables and oils ranged from 91 to 104%.
A. O. JONES

3994. **Determination of vitamin A in nutritious beverages with high extract content.** W. Kleber, A. Hartl and P. Schmid (Wissenschaftl. Sta. f. Brauerei, Munich, Germany). *Brauwissenschaft*, 1959, **12** (12), 274–279.—The following procedure is designed for samples containing substances that interfere with the application of the usual methods. *Procedure*—Dilute the sample (containing 10 to 40 μg of vitamin A) to 100 ml, add 4 *N* HCl (5 ml) and extract with diethyl ether (3 × 25 ml). Extract the ether soln. with 0·2 *N* NaOH (3 × 25 ml) and (after washing with water and drying with Na_2SO_4) evaporate it to dryness. Dissolve the residue in *iso*propyl alcohol (10 ml). (The extractions and evaporation must be carried out under N.) Determine the extinction of the final soln. in a 1-cm cell at 326 mμ (with a blue filter) before and after destruction of the vitamin by irradiation for 2 hr. with u.v. light. The difference between the first and second values multiplied by 1525 gives the percentage of vitamin A (as the acetate) in the soln. examined, from which the content of the original sample can be calculated. P. S. ARUP

3995. **Vapour chromatography applied to the resins and essential oils of hops.** — Cassuto (École de Brasserie, Nancy). *Brasserie*, 1960, **15**, 40–45; 64–70.—Alkaline hydrolysis of the soft resins of hops precipitable by Pb acetate (α-acids) liberates 4-methylpent-3-enoic acid, and an attempt was made to estimate this acid by vapour chromatography on a silicone - stearic acid column. The peak obtained did not permit of satisfactory measurement, but the acid issuing from the column was identified as its *p*-bromophenacyl ester, the amount corresponding to the weight of α-acids taken. Oxidation of α-acids with H_2O_2 in alkaline medium similarly gave identifiable peaks for *iso*butyric, *iso*valeric, 2-methylbutyric and 4-methylpent-3-enoic acids, but the areas could again not be measured. From the amounts of *p*-bromophenyl esters found, the α-acid mixture was estimated to consist of 60% of humulone, 20% of cohumulone and 20% of adhumulone. Gas chromatography of the terpenes and sesquiterpenes of the essential oils of hops, after first separating from oxygenated compounds on a column of silica gel, was carried out with a column of Apiezon at 180° and He as carrier gas. A chromatogram with 13 peaks, similar to those obtained by other workers, but better separated, was obtained. Of these, six were identified as due to myrcene, α-pinene, limonene, β- (or γ-)caryophyllene, humulene and methyl nonyl ketone; β-pinene and farnesene could not be found, or were present in amounts too small to be detected with the apparatus used. C. L. HINTON

3996. **Reducible disulphides in beer. I. Analytical method.** M. W. Brenner, J. L. Owades, G. J. Schapiro and S. Laufer (Schwarz Lab., Inc., Mt. Vernon, N.Y., U.S.A.). *Proc. Europ. Brew. Conv., Rome*, 1959, 239–245 (in English).—An electrolytic de-salting apparatus, used by Benesch and Benesch (*Biochim. Biophys. Acta*, 1957, **23**, 643) for the determination of disulphides by electrolytic reduction to thiols, and similar to that of Consden *et al.* (*Biochem. J.*, 1947, **41**, 490), has been applied to the analysis of beer. The apparatus and procedure are described. The sample (2 ml) is treated with 2% Na_2SO_4 soln. (2 ml) and 1 drop of *n*-decanol to prevent foaming, and reduced for 15 min. at 5 V. An aliquot (2 ml) of this soln. is transferred to a beaker containing *M* tri(hydroxymethyl)methylamine (4 ml), *M* HNO_3 (3·2 ml), *M* KCl (0·3 ml) and 0·3% gelatin soln. (1 ml) and immediately titrated amperometrically with 0·002 *M* $AgNO_3$, with a rotating platinum electrode and mercury - mercuric oxide - barium hydroxide reference electrode (Brenner *et al.*, *Anal. Abstr.*, 1958, **5**, 2396; 1959, **6**, 3216). Small increments of titrant are added at regular intervals until three successive additions cause equal displacements of the galvanometer needle. The end-point is determined by extrapolation of the graph of galvanometer deflection *vs.* vol. of titrant back to zero current. A correction is applied for the amount of thiol present in the beer before reduction. The method is standardised with oxidised glutathione. Results for American and European beers are reported. R. E. E.

3997. **Determination of ascorbic acid in beer.** T. A. Downey (Tech. Service Dept., Chas. Pfizer and Co., Inc., Brooklyn, New York, U.S.A.). *Brauwissenschaft*, 1959, **12** (12), 286–289.—Accurate results, unaffected by the presence (in the usual concn.) of metabisulphite or by the reductones of beer, can be obtained for small (residual) amounts of ascorbic acid by the application of the Hochberg method according to the directions given here. The vol. of the sample is chosen to give a concn. of 2 to 6 μg of the acid per ml in the final soln. for spectrophotometric measurement. The extinction is measured 5 and 10 sec. after the mixing of the reagents with the test soln., and the results are corrected to the extrapolated value for 0 sec. A blank value is obtained for the same beer without ascorbic acid, and subtracted from the last-mentioned value. P. S. Arup

3998. **Hop analysis, cohumulone factor and the bitterness of beer: review and critical evaluation.** M. Meilgaard (Alfred Jørgensen Lab. for Fermentation, Copenhagen, Denmark). *J. Inst. Brewing*, 1960, **66** (1), 35–50.—The sampling of a consignment of hops is discussed, and a simplified procedure, based on statistical considerations, is proposed. The exchange of moisture between the sample and the ambient air is discussed, and a procedure for moisture determination, involving the use of plastic bags at all stages of sampling, is described. The bittering power of hops is related to the conversion of the α-acids into their *iso* derivatives during the brewing process, and it is pointed out that the utilisation of cohumulone is almost twice that of humulone and adhumulone, so that the percentage of cohumulone must be considered when calculating the bittering power of a sample of hops from its α-acid content. Suitable formulae are given, and methods for the determination of bittering power are discussed. The α-acids deteriorate during storage, to produce substances which, though bitter, do not appear in the analysis, and methods of calculating the true bittering power from the α-acid content of stored hops are described. It is suggested that the conductimetric lead titration method of analysis of the $CHCl_3$ extract of the hops (Trolle and Djurtoft, *Brauwissenschaft*, 1958, **11**, 283) gives a better measure of the bittering power of stored hops than the conventional methods of analysis. R. E. E.

3999. **Chromatographic - polarimetric determination of the α-bitter acids content of hops.** H. Bausch, H. Wolter and D. Sommer (Inst. f. Gärungschem. u. Landwirtschaftl. Technol., Humboldt-Univ., Berlin, Germany). *Nahrung*, 1959, **3** (5–6), 501–514.—The chromatographic - polarimetric method of Verzele (*Wallerstein Labs Commun.*, 1957, **20**, 7) has been evaluated and shown to give occasional low results compared with the methods of Wöllmer (*Wochschr. Brau.*, 1930, **47**, 521) and Gough (*J. Inst. Brewing*, 1956, **62**, 9). If double the volume of diethyl ether specified by Verzele is used as eluent, the agreement is satisfactory. A modification of the Verzele method is proposed in which ethyl acetate, through which SO_2 has been bubbled for 15 min., is used as eluent. The effects of moisture in the solvent and of elution period on the optical rotation of the eluate are discussed. Typical results are tabulated. The standard error is ±0·19% and the time required for a determination is 30 min. S. M. Marsh

4000. **Iodoform reaction of hop bitter acids and their conversion products in wort and beer as a basis for a new method of quantitative determination.** E. Mikschik (Braueri Schwechat A.-G., Schwechat/Wien, Österreich). *Proc. Europ. Brew. Conv., Rome*, 1959, 138–148 (in German).—When an alkaline soln. of hop bitter acids is allowed to react with iodine under suitable conditions, CHI_3 is pptd. It is shown that the acyl groups of co- and ad-humulone, but not those of humulone, are concerned in the formation of CHI_3 and that, when the α-acids are boiled, they are converted into a product having an additional acyl group, which also yields CHI_3. *Procedure for co- plus ad-humulone*—Dissolve the sample of α-acids in 0·5 *N* NaOH (40 ml, satd. with CHI_3) and add dropwise (1 to 2 drops per sec.), with continuous swirling, *N* iodine (4 ml). Set aside for 2 hr., until the supernatant liquid is quite clear. Filter off the CHI_3 in a sintered-glass crucible, wash with H_2O (10 to 20 ml, satd. with CHI_3 and containing 0·5% of acetic acid) with suction, and dry to constant wt. *in vacuo* over silica gel, in a desiccator in which is an open vessel containing CHI_3. Then the proportion of co- plus ad-humulone (as a fraction of unity) is given by $WM/H \times 393{\cdot}78$, where *W* is the wt. (mg) of CHI_3, *H* is the wt. (mg) of sample, 393·78 is the mol. wt. of CHI_3, and *M* is the mean mol. wt. of the sample, calculated from the cohumulone content of the α-acids for the particular variety of hop under examination. To determine this, dissolve the Pb salt of the mixed α-acids (*P* mg) in glacial acetic acid at 40° to 50°, then remove Pb from the soln. with 50% KI soln. Remove acetic acid from the filtrate by distillation *in vacuo*, and treat the residual soln. as described above. Then co- plus ad-humulone (%) = $143 \times W/P$. *Procedure for the "bitter value" of beer*—Mix de-gassed beer (100 ml) with H_2O (100 ml) and evaporate on a hot-plate to ≃ 40 ml. Transfer the liquid to a 100-ml flask, saturate with CHI_3 by adding an excess of an aq. suspension of CHI_3,

adjust the pH to 7 to 8 with 30% NaOH soln., make up to vol., mix and filter. Into each of six centrifuge tubes, charged with 0·5 ml of 30% NaOH soln., transfer 10 ml of the filtrate, then to each tube add 0·75 ml of *N* iodine as described above. After 2 to 3 min., centrifuge at 4000 r.p.m. for 2 min., then add 0·5% aq. acetic acid soln. satd. with CHI_3 (10 ml) and 0·1 *N* $Na_2S_2O_3$ (0·5 ml). Mix well, collect the ppt. in a sintered-glass crucible, and wash, dry and weigh as described above. Then remove CHI_3 from the co-pptd. impurities by washing with *n*-hexane (3 × 10 ml) and dry and weigh the crucible. The wt. of pure CHI_3 (*W* mg) is obtained by difference. Then bitter value (mg per litre) = 7·58 *W* (for true *iso*humulone use the factor 5·05). The results for bitter value are in satisfactory agreement with those by the method of Kolbach and Vogl (*Wochschr. Brau.*, 1933, **50**, 421). R. E. E.

4001. **Mass-spectrometric studies of hop bitter substances.** S. Brohult, R. Ryhage, L.-O. Spetsig and E. Stenhagen (Forskiringslab. LKB, Appelviken, Sweden). *Proc. Europ. Brew. Conv., Rome*, 1959, 121–127 (in English).—The results are reported of a mass-spectrometric study of the bitter substances separated by partition chromatography, *viz*, humulones (α-acids), lupulones (β-acids) and the recently isolated hulupulones (γ-acids) (Spetsig *et al.*, *Proc. Europ. Brew. Conv., Copenhagen*, 1957, 22). The hulupulones were extracted from Hersbrucker hops by reversed-phase partition chromatography on hydrophobic Hyflo Super-Cel by the method of Silk and Hahn (*Anal. Abstr.*, 1954, **1**, 970) as modified by Spetsig and Steninger (*J. Inst. Brewing*, 1956, **62**, 333). The instrument used was a high-resolution mass spectrometer with a heated inlet system (Ryhage, *Ark. Kemi*, 1959, **13**, 475), the resolution extending up to *M/e* 500. The mass range from 12 to 300 could be scanned in 4 min. Mass spectra for lupulone, humulone, hulupulone and dihydrohulupulone are presented and discussed. R. E. E.

4002. **Detection of wine from hybrid grapes in wine produced from Vinifera grapes.** H. Rentschler (Eidg. Versuchsanstalt f. Obst-, Wein- und Gartenbau, Wädenswil, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (6), 533–540.—The colour of red wines is caused by the presence of anthocyanins that are characteristic for the species of grapes used in their production. The identification of the pigment in a given wine sample, therefore, makes it possible in many cases to prove the presence of an admixture of foreign wines. Thus malvidine diglucoside, which is characteristic of American wine, can be identified by paper chromatography. The wine (0·05 ml) is applied as a streak to Whatman No. 4 filter-paper; the chromatogram is developed by the ascending method with 1% formic acid for ≃ 20 min. If the chromatogram is viewed under u.v. light a brick-red fluorescence at an R_F of ≃ 0·4 is characteristic of the presence of malvidine diglucoside. The pigments of red wine that is light in colour can be concentrated by adsorption on charcoal followed by extraction with boiling 10% ethanolic formic acid. The eluate is concentrated *in vacuo* (1 to 2 ml) and then used for chromatography. The test may not be effective for wines more than a few years old. S. Baar

4003. **Flame-photometric determination of potassium and sodium in wine.** W. Diemair and C. Gundermann (Univ. Inst. f. Lebensmittelchemie, Frankfurt a. M., Germany). *Z. LebensmittUntersuch.*, 1959, **111** (2), 120.—In a previous paper (*cf. Ibid.*, 1959, **109**, 469), a 1:10 dilution of the sample for the flame test was recommended; greater accuracy is attained with a 1:100 dilution. The max. concn. per 100 ml of the standard soln. should be 2·5 mg for K and 1 mg for Na. Calibration graphs are given for the determination of K and Na. P. S. Arup

4004. **Determination of volatile acids in wine.** H. Eschmann (Kant. Lab., Zug, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (6), 541–552.—Conditions are studied for the recovery of volatile acids in wine by steam-distillation. The following routine procedure is recommended. Wine (50 ml), NaCl (10 g) and water (60 ml) with a few drops of anti-foaming agent are placed in a 250-ml flat-bottomed distillation flask. The contents are first warmed to expel CO_2 and then the flask is connected to an apparatus consisting of a splash-head and a vertical double-surface condenser; 100 ml of distillate is collected and titrated with 0·1 *N* NaOH. S. Baar

4005. **Simple quantitative polarographic determination of lead in grape must and wine.** E. Gilbert and H. Grohmann (Chem. Untersuchungsamt, Speyer, Germany). *Dtsch. LebensmittRdsch.*, 1959, **55** (12), 300–303.—Polarography is carried out with a soln. of the ashed sample in 2 *N* HCl (2 ml). This is diluted to 5 ml with water, and *N* LiCl (1 ml), 0·1% gelatin soln. (1 ml) and (to obviate interference by Fe, Cu and Zn) 0·5% $K_4Fe(CN)_6$ soln. (1 ml) are added. The lead content of 20 samples investigated was from 0 to 0·17 mg per litre. E. C. Apling

4006. **Paper chromatography of lipid substances.** Č. Michalec and C. Soběslavský (Lab. Metabolism Proteins, Med. Fac., Charles' Univ., Prague). *Chem. Listy*, 1959, **53** (11), 1170–1230.—A review is given, with 246 references. J. Zýka

4007. **Determination of the iodine value of fats and oils by means of N-bromosuccinimide. I. Monounsaturated fatty acids.** A. Jovtscheff (Chem. Inst., Bulg. Acad. Sci., Sofia). *Nahrung*, 1959, **3** (2), 153–160.—The fatty acid (0·12 to 0·15 g) is treated with 20 to 25 ml of N-bromosuccinimide (**I**) reagent (18 g dissolved in 1 litre of glacial acetic acid) and the mixture is set aside in the dark at room temp. for 1 hr. Then 20 to 25 ml of 10% KI soln. and ≃ 100 ml of water are added and the iodine liberated by the excess of **I** is titrated with 0·1 *N* $Na_2S_2O_3$. The method of calculation is described. The coeff. of variation of the iodine value is ± 0·8%. The results agree well with those obtained by Kaufmann's method. S. M. Marsh

4008. **Distinction between refined and unrefined olive oils.** E. Lauber (Gesundheitsamt, Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (6), 553–566.—Raw oils have a higher electrical conductivity because of their greater acidity and the presence of phosphatides. A special conductivity cell is used and precise constructional details of the apparatus are given. A sample of 35 to 40 ml is required and the measurements are made at exactly 100°. Absorption curves over the range of 450 to 750 mμ showed that the extinction at 500 mμ was also a measure of the degree of refining of the oil. A peak at 670 mμ is caused by chlorophyll and low values are given by refined olive oils. S. Baar

4009. **Application of gas - liquid partition chromatography to the quantitative determination of monoglycerides.** A. G. McInnes, N. H. Tattrie and M. Kates (Div. Appl. Biol., Nat. Res. Council, Ottawa, Canada). *J. Amer. Oil Chem. Soc.*, 1960, **37** (1), 7–11.—A direct and rapid quant. separation of the fatty-acid components of monoglycerides (C_8 to C_{18} acids) in mixtures of glycerides can be made by converting the former to the corresponding allyl esters, followed by vapour-phase chromatography. The monoglyceride is treated with mesyl chloride in pyridine and the dimesyl derivative is decomposed with NaI in acetone at 100°. Aliquots of the resulting allyl ester mixture are then separated by a column of Apiezon M on Celite 545 (1:4, w/w) at 240°. Peak heights of C_8 to C_{12} esters and peak areas of C_{14} to C_{18} esters are proportional to the weight concentration. Analyses of monolaurin and monomyristin mixtures of known composition gave 96 to 98% recovery of the allyl esters. The method can be applied to both α- and β-monoglycerides. (18 references.) P. M. KINGSTON

4010. **Standardised methods for use in the fat and wax industry. XXIX. Analysis of technical fatty acids (2).** Dtsch. Gesellschaft für Fettwissenschaft (Münster, Westphalia). *Fette, Seif., Anstrichmitt.*, 1959, **61** (12), 1211–1216.—Assay methods for the quality control of fatty acids used in industry are described. S. BAAR

4011. **Determination of unconjugated *trans* unsaturation in C_{18} acids and esters from natural sources.** B. Cleverley (Dominion Lab., D.S.I.R., Wellington, New Zealand). *Anal. Chem.*, 1960, **32** (1), 128–130.—Difficulties due to spectral interference in the infra-red determination of unconjugated *trans* unsaturation in C_{18} fatty-acid or ester mixtures from natural lipids, when the differential method is used for measuring the extinction of the *trans* peak at 965 cm^{-1}, have been overcome. A procedure is described for achieving compensation so that the overlapping bands around 965 cm^{-1} can be separated graphically. The *trans* unsaturation thus determined is expressed as a percentage of elaidic acid or methyl elaidate. Results are outlined and discussed. S. M. MARSH

4012. **Ultra-violet spectral studies on the quantitative determination of linoleic and linolenic acids by conjugation.** C. Franzke (Inst. f. Lebensmittelchem. u. -technol., Humboldt Univ., Berlin, Germany). *Nahrung*, 1959, **3** (3–4), 238–251.—The isomerisation of linoleic and linolenic acids at 180° with a reagent prepared by treating ethanediol (500 ml) with KOH (45 g) at 190° for 15 min. under O-free nitrogen, has been studied. The extinction coeff. of the resulting mixtures were determined. The effects of isomerisation time, size of sample, temp. of reaction and solvent have been studied. Good results are obtained only under carefully controlled conditions. Isomerisation with potassium *tert.*-butoxide shows promise as an alternative method. It is preferable to use as standards natural fatty acids isolated by chromatography rather than those isolated by chemical means (bromine addition). S. M. MARSH

4013. **Paper chromatography in the field of fats. XXXIX. Quantitative analysis of fatty-acid mixtures containing palmitoleic acid.** H. P. Kaufmann, H. Schnurbusch and Z. E. Shoeb (Dtsch. Inst. f. Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1960, **62** (1), 1–5.—A procedure is described for the separation and determination of fatty acids in mixtures containing palmitoleic, myristic and linoleic acids, which have the same R_F values. The mixture is chromatographed on paper with the system undecane/acetic acid - methyl cyanide. The spots are made visible by treating the paper with Cu acetate to form the copper soaps, and, after removal of the excess of copper salt, with dithio-oxamide. The brown spots thus obtained can be evaluated photometrically or eluted with benzene and re-chromatographed. The spot containing the palmitoleic, myristic and linoleic acids is transferred directly with the aid of benzene to the starting line of a second paper strip. The transferred acids are hydrogenated and the corresponding saturated acids (palmitic, myristic and stearic acids, respectively) can then be separated chromatographically. Animal fats have been analysed in this way and the iodine value and thiocyanogen value calculated from the composition found agree with those determined on the original mixture. G. BURGER

4014. **A new semi-micro complexometric method for the determination of propyl gallate in fats.** B. A. J. Sedláček (Abt. f. Lebensmittelhygiene, Inst. f. Ernährungsforschung, Prague, Czechoslovakia). *Z. LebensmittUntersuch.*, 1959, **111** (2), 108–111.—This method depends on the pptn. of the propyl gallate (**I**) from aq. soln. as the Hg^{II} complex, and the complexometric titration of the Hg in the ppt. *Procedure*—Extract a soln. of the sample (25 g) in light petroleum (b.p. ≯ 60°, 150 ml) with water (5 × 20 ml) at 50°. Boil the aq. extract under reflux with aq. 10% Hg acetate soln. (2 ml) and aq. 10% Na acetate soln. (0·5 ml) for 10 min., cool, filter, and wash the ppt. free from Hg acetate. Dissolve the ppt. in 1% HCl (10 ml) followed by water (100 ml), add to the soln. 0·005 *M* EDTA (25 to 50 ml according to the amount of **I** expected) and neutralise with 1% NaOH soln. After the addition of 2 ml of a buffer soln. (containing NH_4Cl and aq. NH_3) and a little Eriochrome black T, titrate the residual EDTA with 0·005 *M* $ZnSO_4$ to a red colour. The method is valid for the titration of 0·5 to 7 mg of **I**, and is more accurate than other available methods, the error being ≯ 0·24%. P. S. ARUP

4015. **Modification of the Roe - Kuether method for the determination of ascorbic acid.** K. Szőke (Inst. f. Ernährungswissenschaft, Budapest, Hungary). *Nahrung*, 1959, **3** (3–4), 292–298.—The original procedure (*J. Biol. Chem.*, 1943, **147**, 399) has been modified by dissolving the osazone in ethanol instead of in 85% H_2SO_4. The sample soln. (5 to 80 μg of ascorbic acid) (1 ml) is treated with 0·15 ml of bromine water and after 10 min. the excess of Br is removed with N. The mixture is then diluted to 4 ml with 4% trichloroacetic acid soln. and treated with 1 ml of 2% 2:4-dinitrophenylhydrazine soln. in 9 *N* H_2SO_4, and maintained at 37° for 3 hr. After cooling, the pptd. osazone is dissolved by addition of 5 ml of 96% ethanol. The extinction of the soln. is then measured at 530 mμ after 20 min. Typical results are quoted and the method has been successfully applied to fresh, frozen and dried materials. S. M. MARSH

4016. **Influence of flavonoids on the colorimetric determination of L-ascorbic acid with 4-methoxy-2-nitroaniline.** V. Davídek and E. Davídková

(Zentralforschungsinst. f. Lebensmittelind., Prague, Czechoslovakia). *Nahrung*, 1959, **3** (5–6), 515–519. —It is shown that the colorimetric method of Schmall *et al.* (*Anal. Chem.*, 1953, **25**, 1486) is not reliable for highly coloured extracts and materials or those rich in pectin. The presence of an 8-fold excess of flavonoids causes the colour to change from blue to brown-red. With extracts rich in pectin, the pectic substances pptd. on the addition of alcohol adsorb some of the colour, thus leading to low results. S. M. MARSH

See also Abstracts—**3647**, Zinc in org. material. **3877**, Sugars in foods. **3896**, Nicotinamide in presence of nicotinic acid. **3928**, Components of irradiated ergosterol. **3959**, **3960**, Vitamin B_{12} in pharm. prep. **3973**, Analysis of saccharin. **3974**, Determination of saccharin. **3978**, Toxicological analysis of foods. **4086**, Colour standards for sugar products.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

4017. **Modified nitrogen dioxide reagent for recording air analysers.** R. E. Saltzman (Public Health Service, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1960, **32** (1), 135–136.—A study has been made of the effect of varying the concn. of the three components of the reagent used in the Saltzman modification of the Griess-Ilosvay reaction for application to a recording air analyser. The best compromise of cost, colour intensity and colour-development time is obtained with a reagent containing 0·5% of sulphanilic acid, 5% of acetic acid and 0·005% of N-1-naphthylethylenediamine dihydrochloride. K. A. PROCTOR

4018. **Determination of aniline vapour in air.** E. V. Gernet and A. A. Russkikh. *Zavod. Lab.*, 1960, **26** (1), 58.—The air is passed through a reagent paper prepared by soaking a filter-paper in a 5% soln. of *p*-dimethylaminobenzaldehyde in 50% acetic acid soln. (by vol.) and blotting with filter-paper so that the moisture content of the paper is $\simeq$ 0·5% of its wt. The colour (yellow) produced by aniline is compared with an artificial scale of standards covering the range from 0·03 to 3 μg of aniline. G. S. SMITH

4019. **Industrial use of pentachlorophenol and sodium pentachlorophenoxide and their determination in the atmosphere.** V. Podolský and E. Vizváry (Inst. Hyg. and Ind. Diseases, Bratislava, Czechoslovakia). *Pracovní Lékařství*, 1959, **11** (9), 461–465.—A semi-quant. spot method is developed, based on the reaction of pentachlorophenol (**I**) with Cu^{II} acetate. *Procedure*—Absorb the material from the air sample in H_2O (10 ml) and add HCl (1 drop); the sodium salt of **I** is thus converted into **I**; in higher concn. a white ppt. appears. After 2 to 3 min., add light petroleum (0·1 ml) and shake for 10 to 15 sec., till the white turbidity disappears. Set aside for 5 min. and then transfer 10 μl of the light petroleum layer to chromatographic paper, evaporate and moisten with Cu^{II} acetate soln. (0·25%). Compare the red-brown spots immediately with a standard scale. The photometric method of Haskins (*Anal. Chem.*, 1951, **22**, 1672) based on the reaction of **I** with safranine is suitable for a more exact determination of the **I** content of air. J. ZÝKA

4020. **New method for the detection of long-half-life particle aerosols in the atmosphere.** H. Klumb and T. Dahlem (Inst. angew. Phys., Univ., Mainz, W. Germany). *Naturwissenschaften*, 1960, **47** (2), 37–38.—The "aerosol spectrometer" described was made from a prismatic steel block with a hole 18 mm in diam. bored throughout its longitudinal axis. This bore is fitted with a worm core of 10 mm pitch, which converts it into a spiral tube of 6 mm int. diam. through which air is sucked. One long side of this block is then milled away to reveal the internal bore, forming a long slit 5 mm across. This slit is sealed by wrapping the block with plastic foil, carefully fastened to exclude external air. The surface of the foil open to the spiral is coated with petroleum jelly to retain any solid particles. In 24 hr., 150 cu. metres of atmospheric air pass through this tube. At the end of this time the plastic foil is removed and, after allowing 72 hr. for the quenching of radioactive particles of short half-life, it is placed in contact with X-ray autoradiograph film for 24 hr. When developed this shows a clear trace of contact with air in the spiral tube and black spots varying in magnitude between one and four arbitrary units. The distribution of the spots shows maximum intensity half-way along the tube, and a graph shows that all four sizes and the aggregate when plotted have the same contour and the same peak position. The various particles of different activities that have been detected by other methods must be present here, and yet the distribution pattern shows that their deposition on the film is not governed by their mass, but possibly determined by their radioactivity. E. G. CUMMINS

4021. **Further advances in dissolved oxygen micro-analysis. I. Small-scale water-sampling vessels and amperometric titrations.** E. C. Potter and G. E. Everitt (Central Electricity Generating Board, Boiler Corrosion Res. Lab., London). *J. Appl. Chem.*, 1959, **9** (12), 642–645.—Sampling vessels having a capacity of 100 to 250 ml have already been described (*cf.* Potter, *Ibid.*, 1957, **7**, 297). Modified vessels for use with small samples have a capacity of 12·5 ml; to avoid dilution of reagents, a calibrated side-arm is attached to the vessel which will dispense 0·00625 ml of reagent with a precision of $\pm$4%. The accuracy and precision of water sampling and of the amperometric titration are also satisfactory. The precision for complete analysis is $\pm$0·002 p.p.m. of O for 95% confidence limits.

II. Sources of interference. E. C. Potter and G. E. Everitt. *Ibid.*, 1959, **9** (12), 645–650.—The nature of chemical interference with the Winkler reaction is discussed. *cyclo*Hexylamine, morpholine and NH_3 can be tolerated at levels well above those usually found in boiler water. Errors due to Fe^{II} and to hydrazine are overcome by passing the sample through Zeo-Karb 225; the adsorption of hydrazine on the resin has no secondary effect on the O content of subsequent water samples. Interference by SO_3^{2-} is avoided by the use of the reversed-reagents technique.

III. Interference during water sampling. E. C. Potter and G. E. Everitt. *Ibid.*, 1960, **10** (1), 48–56.—Measurements under streamline flow (150 ml per min. at atm. pressure and temp.) show that, because of their permeability (0·01 to 0·28 p.p.m.) to dissolved O, red and black natural-rubber and silicone-rubber tubing must not be used for sampling

H_2O for the micro-determination of dissolved O (see Part II above). Polyethylene tubing is permeable above ≃ 50°, and neoprene tubing is not always impermeable to dissolved O. Poly(vinyl chloride) tubing (white translucent and clear green) should be used only when the internal hydrostatic pressure permanently exceeds 5 lb per sq. in. Nylon appears impermeable up to ≃ 90°. If the sampling device ensures that the water adjacent to the plastics wall is excluded from the sampling manifold, even the most permeable plastics tubing can be used in the sampling line. It cannot be assumed that pick-up of dissolved O is proportional to the length or the wall-thickness of the porous tubing. Diffusion of O through the polymer is probably a dual process in which assisted and resisted permeability are concerned.

P. D. PARR-RICHARD
W. J. BAKER

4022. **Automatic recording of dissolved oxygen in aqueous systems containing surface-active agents.** K. H. Mancy and D. A. Okun (Dept. of Sanitary Engng, Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 108–114.—A dropping-mercury polarograph has been adapted for the continuous recording of dissolved oxygen in an aeration column. The effect of surface-active agents on electrode reaction kinetics has been studied in this closed system which maintains a constant vol. of soln. being aerated.

K. A. PROCTOR

4023. **Micro-determination of calcium in water.** E. Leclerc and G. van Beneden (Univ., Liège, Belgium). *Bull. Cent. Belge Étude et Docum. Eaux*, 1959, (108), 317–319.—The method is based on the pptn. of Ca as $Ca_3(PO_4)_2$ followed by the spectrophotometric determination of the PO_4^{3-}. *Procedure*—The sample, containing 0·025 to 0·1 mg of Ca, is introduced into a 15-ml centrifuge tube, and evaporated, or diluted, to 1 ml, then 1 ml of 20% NaOH soln. is added. After shaking the soln. and allowing it to stand for 5 min., 1 ml of 5% Na_2PO_4 soln. is added. The soln. is again shaken and heated in an oven at 100° for 15 min.; on removal from the oven the soln. is set aside for 1 hr. The ppt. is separated by centrifuging for 5 min., then washed with 5 ml of alcohol soln. (58 ml of ethanol, 10 ml of amyl alcohol and 32 ml of H_2O) with gentle shaking. After being centrifuged and re-washed, the $Ca_3(PO_4)_2$ is dissolved in 10 ml of 20% H_2SO_4, and 2 ml of 5% ammonium molybdate soln. is added. After 5 min., 1 ml of 20% Na_2SO_3 soln. and 1 ml of 0·5% quinol soln. are added with shaking, and the soln. is allowed to stand for 25 min. The extinction is then measured at 650 mμ. The method has a precision of ≃ 10%, whilst commensurate amounts of Al, Fe, Mg and SiO_3 and smaller amounts of $(NaPO_3)_n$ do not interfere. In a modification for sub-micro amounts (2 to 12 μg of Ca), the PO_4^{3-} are determined by measuring the opacity of an alkaloid - molybdophosphate complex (*cf. Bull. Trimestriel du CEBEDEAU*, 1957, **38**, 259).

J. H. WATON

4024. **Determination of calcium and magnesium in water by automatic titration.** J. Haslam, D. C. M. Squirrell and I. G. Blackwell (I.C.I. Ltd., Plastics Div., Black Fan Rd., Welwyn Garden City, England). *Analyst*, 1960, **85**, 27–35.—A direct method for determining calcium and magnesium in the same sample of water is described. The acidified sample is boiled to remove CO_2, and NaOH soln. and a known vol. of 0·004 *M* mercuric nitrate are added. The liquid is then titrated in the automatic recording titrimeter with 0·02 *M* EDTA (disodium salt) until the record shows that the end-point for Ca has just been passed. The liquid is then acidified (1 ml of *N* HCl), *M* aq. NH_3 is added, and titration is continued until the end-point for Ca plus Mg is passed. A bridged calomel reference electrode and mercury - silver amalgam indicator electrode are used. A slight modification for determination of the Ca and Mg separately is described.

A. O. JONES

4025. **Determination of fluoride in drinking water with the aid of an ion-exchange resin.** J. A. Fresen, H. van Gogh and J. A. C. van Pinxteren (Farm. Lab. Rijksuniv., Utrecht, The Netherlands). *Pharm. Weekbl.*, 1960, **95** (2), 33–40.—The interference from SO_4^{2-} (> 50 mg per litre) in the determination of F^- with Zr and Eriochrome cyanine R (Pinxteren, *Anal. Abstr.*, 1960, **7**, 3079) can be eliminated by means of anion exchange. *Procedure*—Fill a column (15 cm × 1 cm in diam.) with Dowex 1-X10 (50 to 100 mesh) and keep the resin in H_2O for 2 to 3 hr. Wash it with 100 ml of 4 *N* NaOH and then with H_2O until the percolate is neutral to litmus. Pass 100 ml of 2 *N* HCl through the column and wash the resin with H_2O until the percolate is free from Cl^-. Pass 100 to 130 ml of the F^--containing sample through the column at 2 ml per min., wash the column with 10 ml of H_2O, then elute with 40 ml of 0·1 *N* NH_4Cl adjusted to pH 9·2 with aq. NH_3. Then wash the resin with 10 ml of H_2O and add the washings to the eluate. Make up to 100 ml and determine F^- with Zr and Eriochrome cyanine R as previously described.

M. J. MAURICE

4026. **Ultra-micro determination of iodine in drinking water on the basis of Feigl's catalytic reaction.** E. Jungreis and I. Gedalia (Dept. of Inorg. and Anal. Chem., Hebrew Univ., Jerusalem, Israel). *Mikrochim. Acta*, 1960, (1), 145–149 (in English).—The reaction between chloramine T and 4:4′-tetramethyldiaminodiphenylmethane acetate (**I**) is catalysed by I^-. The reaction product is an unstable blue complex which rapidly fades to a stable green one. The method is based on the measurement of the extinction of the blue complex at the point of maximum absorption. *Procedure*—To the sample soln. (10 ml) add acetate buffer (pH 4·8) (1 ml) and 2 ml of a soln. of **I** (2 ml of a satd. soln. of **I** in acetic acid and 98 ml of water). With this soln. as blank set the photometer at 100% transmittance and add 0·02% chloramine T soln. (1 ml). Mix, and measure the extinction of the soln. at 600 mμ. Calculate the quantity of I^- from a previously prepared calibration curve. The method is suitable for 0·025 to 0·2 μg of I^- in a sample volume of 10 ml. Chloride is without effect, but relatively large quantities of Br^- interfere.

W. T. CARTER

4027. **Determination of traces of cyanide in water by cathode-ray polarography.** J. Hetman (Southern Instruments Ltd., Camberley, Surrey, England). *J. Appl. Chem.*, 1960, **10** (1), 16–18.—Concn. of CN^- in water as low as 0·05 μg per ml can be determined at 25° by a cathode-ray polarograph used with an anodic unit to sweep the potential of the dropping-mercury electrode in the positive direction. The soln. (5 ml), containing 0·1 *M* NaOH as supporting electrolyte, is de-aerated with N for 3 min. and then polarographed anodically at

a starting potential of −0·35 V. More easily measurable waves are obtained when the polarograph is set for derivative current. Large excesses of Cl^- can be tolerated, but free Cl, Br and I, and S^{2-}, must be absent. W. J. BAKER

4028. **Determination of radioactivity in saline waters.** V. J. Sodd, A. S. Goldin and R. J. Velten (Robert A. Taft Sanitary Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 25–26.—Most of the isotopes of interest in sea water can be separated by various pptn. techniques. Many cations can be removed as their sulphides from ammoniacal soln., whilst Sr, Ba and Ra are pptd. as carbonates. Caesium is removed separately with tungstosilicic acid. Recoveries of 90 to 95% are obtained. K. A. PROCTOR

4029. **Determination of individual dihydricphenols in sewage waters and dilute solutions.** Yu. Yu. Lur'e and Z. V. Nikolaeva (VODGEO Inst.). *Zavod. Lab.*, 1959, **25** (10), 1186–1192.—To determine resorcinol, the reaction with catechol and iodine (Willard and Wooten, *Anal. Chem.*, 1950, **22**, 670) is used. Extraction with *n*-butanol is preferred to dissolution in acetone, the molar extinction coeff. (9552) being higher and the period of stability of the colour (10 hr.) being greater. Preliminary distillation or extraction of coloured samples is necessary. A modification of the same reaction can be used for determining catechol. Alternatively, the reaction with $FeSO_4$ (Kursanov and Zaprometov, *Biokhimiya*, 1949, **14**, 467) can be used. To determine quinol the method based on the use of ammoniacal $CdSO_4$ soln. (Vaskevich and Gol'dina, *Zhur. Prikl. Khim.*, 1951, **24**, 1214) is made more selective, either by first determining the contents of resorcinol and catechol, adding sufficient of one of them to make their contents equal, and then determining the extinction against a blank soln. containing known amounts of resorcinol and catechol, or by extraction after oxidation with iodine. G. S. SMITH

See also Abstracts—**3715**, Determination of dissolved O. **3841**, Oil mist in air.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

4030. **Determination of arsenic in treated wood.** W. J. Wilson (Forest Res. Inst., Rotorua, New Zealand). *Anal. Chim. Acta*, 1960, **22** (1), 96–100 (in English).—The method is used for samples containing 0·016 to 0·274% of As_2O_5. *Procedure*—Digest 1 g of the powdered sample with conc. H_2SO_4 (3 ml) and conc. HNO_3 (25 ml), adding further small quantities of conc. HNO_3 if necessary to avoid prolonged charring. Finally heat to the production of fumes of H_2SO_4. Cool, add 1 ml of saturated hydrazine sulphate soln., heat again to fuming for 10 min., cool, and dilute with 40 ml of water. Add ferrous 1:10-phenanthroline perchlorate indicator soln. and titrate from a microburette with 0·01 *N* $Ce(SO_4)_2$ to the production of a faint green colour that is stable for 15 sec. This preliminary titration oxidises reducing substances other than As^{3+}. Add 3 drops of OsO_4 soln. (0·25% in 0·1 *N* H_2SO_4) and titrate the As^{3+}. H. N. S.

4031. **Determination of potassium in fertilisers by flame photometry.** N. Mevel, J. Angot and L. Vanoverberghe (Soc. d'Étud. Chim. pour l'Ind. et l'Agric., Argenteuil, France). *Chim. Anal.*, 1960, **42** (1), 15–23.—The disadvantages of gravimetric methods for the determination of K are discussed. It is shown that the flame photometry of K in fertilisers can be effected if a cool flame (butane - air) is used to suppress interference from foreign cations, and the reading is taken for the 766·5 - 770 mμ doublet with an interference filter. A separate compressor for the atomiser giving a pressure of 2 kg per sq. cm is recommended. The influence of pH is diminished by adjusting the sample soln. to 0·1 *N* in HCl giving a pH of 0·9 to 1·1. Sulphate enhances the emission, and standards for samples containing SO_4^{2-} must also contain SO_4^{2-}. It is shown that foreign cations are not found in fertilisers in sufficient quantities to interfere. It is recommended that after an approx. determination by means of a permanent calibration curve, standards containing nearly the same amounts of K and anions as are present in the sample should be measured at the same time and the result obtained by interpolation. E. J. H. BIRCH

4032. **Spectrophotometric method for the determination of uric acid in poultry excreta.** G. S. Buys and D. J. J. Potgieter (Fac. Agric., Univ. Pretoria). *S. Afr. J. Agric. Sci.*, 1959, **2** (4), 499–506 (in English).—Shake the finely ground and dried excreta (1 g) with 0·5% Li_2CO_3 soln. (100 ml) for 1 hr. at room temp. and centrifuge at 1300 *g* for 10 min. Repeat the extraction by shaking for 30 min. with two further portions of Li_2CO_3 soln. (50 ml each). Dilute the combined extracts to 250 ml with Li_2CO_3 soln., treat a 10-ml aliquot with 6% $HClO_4$ soln. (10 ml) and filter. Add, with constant stirring, 5 ml of the deproteinised extract during 4 min. to 0·1 *M* mercuric acetate in 5% acetic acid soln. (1 ml) heated in boiling water and continue heating for 10 min. in all. Cool in ice-water for 15 min. and centrifuge at 500 *g* for 10 min. Suspend the ppt. in wash liquid [add uric acid (10 mg) to 0·01 *M* mercuric acetate in 1% acetic acid soln. (1 litre), heat at 80° to 90° for 1 hr., set aside overnight and filter] (5 ml) and centrifuge as before. Dissolve the ppt. in 0·5 *M* NaCl in 1% acetic acid soln., dilute to 100 ml and measure the extinction at 290 mμ. Beer's law is obeyed in the concn. range of 0·4 to 1·4 mg of uric acid per 100 ml. The recovery of uric acid is > 98% and the coeff. of variation is ≃ 0·85%. A. R. ROGERS

4033. **Identification of pesticides in mixtures by means of infra-red spectrography.** W. Fischer and U. Uhlich (Inst. f. Pflanzenschutzmittelforsch., Berlin-Dahlem). *Z. anal. Chem.*, 1960, **172** (3), 175–192 (in German).—The infra-red spectra in KBr of a number of pesticides have been studied, and positions and intensities of absorption bands are listed for each compound, together with possible interferences. The materials studied were DDT, γ-hexachlorocyclohexane, dieldrin, aldrin, endrin, parathion, parathion-methyl, malathion, Chlorthion, diazinon, Karathane [2-(1-methylheptyl)-4:6-dinitrophenyl crotonate], Tedion V8 (commercial 2:4:5:4′-tetrachlorodiphenyl sulphone), ferbam, zineb, thiram and captan. It is claimed that mixtures of these can be identified from their spectra. H. M.

4034. **Qualitative analyses of organic phosphorus [pesticides] by colour reactions and simple detection.**

Kansuke Sera, Akira Matsunaga, Akira Murakami, Isao Satō, Kaoru Yamashita and Haruo Yoshimori (Dept. of Legal Med., Kumamoto Univ. Med. School). *Kumamoto Med. J.*, 1959, **12** (3), 193–213.—The value of 13 different colour reactions for the qual. analysis and differentiation of 18 organophosphorus pesticides has been studied. Tests for the detection of phosphorus by ammonium molybdate, of P=S binding by 2:6-dibromo-*p*-benzoquinone-4-chlorimine, of *p*-nitrophenol by NaOH, of the ester radical by hydroxylamine, and of chlorine by $AgNO_3$ have been found to be the most useful. The reactions with 41 other chemicals likely to be encountered in toxicological analysis have also been investigated, and it is shown that it is possible to distinguish these from organophosphorus compounds. R. A. BRENAN

4035. **Qualitative analysis of seventeen organic phosphorus [pesticides] by paper chromatography.** Akira Matsunaga, Akira Murakami, Isao Satō, Kaoru Yamashita, Haruo Yoshimori and Kazuo Shinagawa (Dept. of Legal Med., Kumamoto Univ. Med. School). *Kumamoto Med. J.*, 1959, **12** (3), 214–219.—The detection of organophosphorus pesticides after separation by paper chromatography with butanol - acetic acid - water (4:1:5) as the solvent is described. Details of five spot reactions are given for the detection of P=S binding by 2:6-dibromo-*p*-benzoquinone-4-chlorimine, of *p*-nitrophenol by NaOH, of the ester radical by hydroxylamine, of phosphorus by Hanes and Isherwood's reagent (*Nature*, 1949, **164**, 1107), and of hydroxybenzotriazine by phenyl-1-naphthylamine. A scheme for separation and identification is described. R. A. BRENAN

4036. **Determination of 4-chloro-2-methylphenoxyacetic acid (MCPA), dinitrocresol (DNC) and 2-sec.-butyl-4:6-dinitrophenol [dinoseb], respectively, in mixtures by chromatographic separation.** W. C. E. Bouwman (Plantenziektenkundige Dienst, Wageningen, Netherlands). *Chem. Weekbl.*, 1959, **55** (40), 540–541.—*Procedure*—Prepare a column packing by grinding 20 g of cellulose powder (S. & S. 123) with 16 ml of phosphate buffer soln. (pH 6·8) and transfer this mixture to the column with the aid of the eluent (a 1:1 mixture of $CHCl_3$ and ether, shaken with the buffer); wash the column with 50 ml of the eluent. Add water to a mixture of MCPA and DNC or of MCPA and dinoseb, containing about 250 mg of MCPA, acidify with HCl and extract several times with ether. Wash the ether extracts with water, dry over anhyd. Na_2SO_4, filter and distil. Dissolve the weighed residue in exactly 50 ml of $CHCl_3$, transfer 1 ml to the column and elute with the $CHCl_3$ - ether mixture. Collect the eluate in 10-ml portions. Shake the yellow fractions containing DNC or dinoseb (usually the third to seventh fractions) with 120 ml of 0·33 *N* NaOH, and make up to 200 ml. Dilute the soln. with 0·2 *N* NaOH so that the concn. of DNC or dinoseb is about 1 to 1·5 mg per 200 ml and measure the extinction in a 1-cm cell at 370 mμ for DNC or at 375 mμ for dinoseb against a blank of 0·2 *N* NaOH. Distil the subsequent eluted fractions until no visible residue remains (after about 40 to 50 fractions). Dissolve all the residues in ethanol and dilute to 50 ml with ethanol. Measure the extinctions at 287, 282, 278 and 270 mμ and determine MCPA by the method of Grabe (*Acta Chem. Scand.*, 1950, **4**, 806). The precision of the method is about 3%. M. J. MAURICE

4037. **Determination of mercury in organic fungicides by the dithizone method.** Jun Kanazawa and Rokuro Sato (Agric. Chem. Inspect. Sta., Kodaira, Tokyo). *Japan Analyst*, 1959, **8** (7), 440–444.—The method of Miller *et al.* (*Anal. Chem.*, 1951, **23**, 1286) was applied to the analysis of fungicides. Organic mercury halides are extracted with dithizone (**I**) in $CHCl_3$ from an acetate buffer of pH 4·5 in the form of RHg^+ (R is an organic radical). The influence of Cu is eliminated by Friedeberg's method (*Ibid.*, 1955, **27**, 305). *Procedure for total mercury*—Heat the sample (1 g) under reflux with HNO_3 (10 ml) and H_2O_2 soln. (30%) (5 ml) and decompose the excess of H_2O_2 with 10% $KMnO_4$ soln.; filter the soln. and decompose the excess of MnO_4^- with 20% hydroxyammonium chloride soln. Determine the Hg in an aliquot ($\equiv \simeq 100$ μg) of the product by the extraction titration method with **I** in $CHCl_3$. *For organic mercury*—Heat the sample (1 g) under reflux with methanol (10 ml), water (100 ml) and glacial acetic acid (10 ml) for 30 min., filter, and wash the residue with hot water. Add 3·5 *N* HCl (18 ml) containing hydroxyammonium chloride (Miller *et al.*, *loc. cit.*) to an aliquot of the filtrate and shake with **I** in $CHCl_3$ (0·01 mg per ml) (10 ml). Wash the $CHCl_3$ layer with 3 *N* HCl (20 ml) and an acetate buffer of pH 4·5 (5 ml), and measure the extinction at 490 mμ. In the presence of Cu, use Friedeberg's method (*loc. cit.*). K. SAITO

4038. **Determination of copper 8-hydroxyquinolinate used as fungicide and antiseptic.** Kenji Motojima and Hiroshi Hashitani (Dept. Chem., Japan Atomic Energy Res. Inst., Tokai, Ibaragiken). *Japan Analyst*, 1959, **8** (8), 526–531.—The determination of 8-hydroxyquinoline (**I**) adsorbed on textile fibres (*cf.* Darbey, *Amer. Dyest. Rep.*, 1953, **42**, 453) was modified by the use of 0·1 *M* H_3PO_4 in place of HCl; the interference from Fe is thus eliminated. In the presence of coloured org. substances, the Cu - **I** complex is extracted with $CHCl_3$ in the presence of excess of Cu^{2+} before measuring the extinction. *Procedure*—Heat the textile sample (1 g) with 0·1 *M* H_3PO_4 (20 ml) on a water bath, then filter and make the filtrate up to 100 ml. Measure the extinction at 360 mμ. When the H_3PO_4 extract contains a coloured substance, dilute an aliquot of the extract containing $< 1·5$ mg of **I** to 35 ml, add $CuSO_4$ soln. (0·1%) (3 ml) and ammonium acetate soln. (2 *M*) to give a pH of 5, and shake with $CHCl_3$ (20 ml); measure the extinction at 410 mμ. K. SAITO

See also Abstracts—**3845**, Quaternary ammonium compounds in animal feeding-stuffs. **3871**, Sulphur in plant tissues. **3993**, Hexachloro*cyclo*hexane residues in foods.

5.—GENERAL TECHNIQUE AND APPARATUS

General

4039. **Weighing vessels for microchemical analysis.** British Standards Institution (2 Park St., London, W.1). B.S. 1428 : Part H1:1960. 8 pp.—Five types are specified.

4040. **Simple automatic pipette.** H. H. Kreutzer (Lab. R. K. Ziekenverpleging, Hilversum, Netherlands). *Chem. Weekbl.*, 1959, **55** (51), 746–748.—A glass pipette (*e.g.*, 1 ml) is bent to an acute angle above the bulb; the two ends are drawn out to a suitable internal diameter, and cut off so that when the pipette is mounted by means of a rubber stopper on a polyethylene bottle, the ends are in the same horizontal plane. Filling and emptying are carried out by suction and pressure is applied by manipulation of the bottle, the excess of liquid over that required to fill the pipette falling into the bottle. Pipettes with a volume of less than 0·2 ml are treated with silicone. The coeff. of variation of the volume delivered ranges from 0·5% for a volume of 0·08 ml to 0·1% for one of 3 ml. These pipettes may be used with poisonous reagents.
M. J. MAURICE

4041. **Multiple pipetting device.** L. Shapiro and W. W. Brannock (U.S. Geol. Survey, Washington, D.C., U.S.A.). *Chemist Analyst*, 1959, **48** (4), 100.—A device for accurately pipetting up to 30 aliquots of liquid simultaneously is described.
G. S. ROBERTS

4042. **Micro-nitrometer (Pregl type).** British Standards Institution (2 Park St., London, W.1). B.S. 1428: Part D3: 1960. 12 pp.—Details of construction and the method of use are described.

4043. **New apparatus for separation of chemical compounds by liquid - liquid extraction.** P. K. Hietala (Biochem. Inst., Helsinki, Finland). *Acta Chem. Scand.*, 1960, **14** (1), 212–214.—A new type of counter-current apparatus with 100 or more distribution tubes and a continuous solvent flow has been designed. The apparatus can be run with either flowing upper phase or flowing lower phase. This can be done with successively smaller amounts of both phases.
N. E.

4044. **Some quantitative remarks on extraction equilibria. III.** M. Oosting (Anal. Res. Inst. T.N.O., Rijswijk, Netherlands). *Anal. Chim. Acta*, 1959, **21** (6), 505–510 (in English).—The equations developed in earlier work (*Ibid.*, 1959, **21**, 301, 397) are applied to the calculation of the conditions for separations by extraction. It is shown that it should be possible to separate, by $CHCl_3$ extraction of 8-hydroxyquinolinates, UO_2^{2+} from Cu^{2+} between pH 2·57 and pH 2·71, UO_2^{2+} from Fe^{3+} between pH 1·76 and pH 2·71, and Fe^{3+} from Al^{3+} between pH 1·76 and pH 2·70, whereas Al^{3+} and UO_2^{2+}, and UO_2^{2+} and Th^{4+} cannot be separated. The criterion for separation is $\lessdot$ 98% extraction of one component and $\gtrdot$ 2% of the other.
T. R. ANDREW

4045. **Manifold for solvent evaporation.** J. R. W. Miles (Entomology Lab., Res. Branch, Canada Agric., Chatham, Ontario, Canada). *Chemist Analyst*, 1959, **48** (4), 100–101.—A distributor head from a 6-cylinder car engine has been modified to produce a manifold suitable for passing gas through 6 glass flasks simultaneously.
G. S. ROBERTS

4046. **Modified analyser for the determination of small amounts of oxygen in gases.** V. Pour and J. Müller (Inst. Inorg. Chem., Acad. Sci., Prague). *Chem. Průmysl*, 1959, **9** (12), 630–632.—A modification of the colorimetric analyser (*cf.* Šourek and Rečka, *Anal. Abstr.*, 1959, **6**, 5051) is described and illustrated; this enables 3×10^{-4} to 2×10^{-2} % by vol. of oxygen to be determined in a mixture of nitrogen and hydrogen. The apparatus contains a specially adapted absorber to allow for the continuous dosing of the absorption soln. The apparatus responds very rapidly to changes of oxygen concn.
J. ZÝKA

See also Abstract—**3788**, New simple nitrometer.

Chromatography, ion exchange, electrophoresis

4047. **Automatic fraction collector for readily flammable substances.** J. Poláček (Inst. Phys. Chem., Acad. Sci., Prague). *Chem. Listy*, 1960, **54** (1), 74–76.—The eluate flows from a siphon into a funnel, to the stem of which is attached a bell floating in mercury contained in an outer chamber, into which an electrode is fused below the surface of the mercury. As the eluate rises in the funnel it pushes the mercury up round the bell until it makes contact with the other electrode causing the movement of the platform. Diagrams are given.
J. ZÝKA

4048. **Clathrate compounds in chromatography.** W. Kemula and D. Sybilska (Polish Acad. Sci., Warsaw). *Nature*, 1960, **185**, 237–238.—A column filled with water-insol. tetra-(4-methylpyridino)-nickel dithiocyanate, prepared by the method of Schaeffer *et al.* (*J. Amer. Chem. Soc.*, 1957, **71**, 5870), gave satisfactory separation of isomeric nitrophenols, nitroanilines, chloronitrobenzenes and nitrotoluenes. In all cases quant. separation of *ortho* from other isomers was obtained by using a γ-picoline - water - KSCN system as the mobile phase. The *o*-isomers were found in the first fraction of the eluate and were determined polarographically. The *m*- and *p*-isomers can be eluted with more concentrated soln. of KSCN and γ-picoline. Nitroaliphatic isomers were successfully separated by using a modified column filling.
G. P. COOK

4049. **An improved multi-sheet frame for two-dimensional paper chromatography.** P. R. Watt and J. Green (Walton Oaks Exper. Sta., Tadworth, Surrey). *Chem. & Ind.*, 1959, (49), 1543–1544.—A design for a frame is illustrated that will accept 20 cm × 20 cm papers without punched holes, can be loaded rapidly and keeps the papers flat at all stages, while a closer spacing than usual can be used.
N. E.

4050. **Modified chromatographic micro-applicator.** D. Kirman (Med. Res. Lab., Veterans Admin. Hosp., East Orange, N.J., U.S.A.). *Amer. J. Clin. Path.*, 1959, **31** (5), 410–411.—The construction of a simple and inexpensive micro-applicator for use in large-scale chromatographic studies is described. The method of application is accurate and time-saving and spots of uniform diameter are delivered, enabling separations to be more clearly defined.
P. NICHOLLS

4051. **De-salting of paper chromatograms by cutting off the starting spots.** K. Lindner (Staatl. Inst. f. Ernährungs- u. Verpflegungswissenschaft, Budapest, Hungary). *Nahrung*, 1959, **3** (3–4), 299–304.—Salts and other interfering substances are eliminated by removing the chromatogram from the tank after the solvent front has travelled 15 to 20 cm, drying it and cutting off the starting spots that contain the impurities. The chromatography is then re-commenced and continued to completion.

The method has been successfully applied in the analysis of amino acids from cows' milk, human milk and blood serum. Typical chromatograms are illustrated and compared with untreated chromatograms. S. M. MARSH

4052. **Stable diazo salts for chromatographic spray reagents.** I. A. Pearl and P. F. McCoy (Inst. of Paper Chem., Appleton, Wis., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 132.—Commercially produced stable diazo salts of some aromatic amines have been shown to be suitable spray reagents for locating and identifying phenolic compounds and aromatic amines on paper chromatograms. A more detailed report is to be published. S. M. MARSH

4053. **Quantitative evaluation of paper chromatograms by reflection measurements.** L. Szalai and S. Szöke (Ungarische Landesanstalt f. Getreide- u. Mehlforschung, Budapest). *Nahrung*, 1959, **3** (7–8), 737–743.—Paper chromatograms of amino acid mixtures are sprayed with 2% ninhydrin soln. and dried at 105°, and the spots are examined directly in a Zeiss Leukometer. The instrument, which measures the total light reflection of almost white surfaces, is described in detail with a diagram. It is simple to use and gives accurate results. Processing operations on the chromatogram are eliminated, errors are considerably reduced, and many amino acids can be determined on a single chromatogram. S. M. MARSH

4054. **Electrostatic discharge methods of zone location for paper chromatographs. IV. Rapid approximate estimations of zone content by static discharge currents.** G. G. Blake (Chem. Dept., Sydney Univ., Australia). *Anal. Chim. Acta*, 1959, **21** (6), 545–548 (in English).—The area of chromatogram of interest is cut out and extracted with H_2O, and the conductivity of the resulting soln. is measured in a device that records the discharge of a charged capacitor through the soln.

V. A chromatographic humidiser. G. G. Blake. *Ibid.*, 1960, **22** (1), 38–40.—When the author's automatic zone locator (*cf. Anal. Chim. Acta*, 1958, **19**, 477) is used in a dry atmosphere it is necessary to humidify the chromatograph to render the spots sufficiently conductive. The apparatus described consists of a channel-shaped strip of polystyrene. In the channel lies a strip of filter-paper, the end of which rests in a water-filled container. Above the paper the channel is widened so that the chromatographic strip can rest, or be drawn through the apparatus, above and parallel to the moist paper without touching it. A strip of glass forms a lid to the trough. T. R. ANDREW
H. N. S.

4055. **Method for determining the area of spots in paper chromatography.** J. S. Knypl and R. Antoszewski (Univ., Lódź, Poland). *J. Chem. Educ.*, 1960, **37** (1), 49.—The chromatogram is placed on a transparent sheet of paper ruled with a mm grid, and backed by a photographic paper or film, the whole being sandwiched between two clean glass plates held by two rubber bands. It is then photographed from the top, using light of a colour complementary to that of the spot being photographed, or white light with a suitable filter. Fluorescent spots can be photographed if the top plate is transparent to u.v. light, and a filter opaque to u.v. light is inserted between the chromatogram and the grid. A suitable exposure time is selected by trial, and the conditions of exposure and photographic development must be kept constant throughout a series of copies. The procedure gives a permanent record, and the method yields results that are independent of contractions or expansions of the photographic paper or film during processing. S.C.I. ABSTR.

4056. **General considerations of the chromatography of inorganic ions on cellulose.** J. Fouarge and G. Duyckaerts (Lab. de Chim. Anal., Univ. de Liège, Belgium). *J. Chromatography*, 1960, **3** (1), 48–57 (in French).—Interpretations are given of the elution mechanisms of alkali metals, alkaline-earth metals and rare-earth metals from cellulose. With phenol satd. with 2 *N* HCl, liquid partition takes place, but with solvents containing methanol the mechanism changes to adsorption, with a corresponding widening of the peaks. The rate of migration is controlled by the amount of "free" water present and, since H^+ bind free water molecules, acids have a retarding effect. When 12 *N* HCl is used as eluent the normal order of elution is inverted owing to the dehydration of the cations by H^+. W. T. CARTER

4057. **Apparatus for the equilibration of columns prior to use in vapour-phase chromatography.** J. A. Cooper, R. Canter, F. L. Estes and J. H. Gast (Dept. of Biochem., Baylor. Univ. Coll. of Med., Houston, Tex., U.S.A.). *J. Chromatography*, 1960, **3** (1), 87–90.—The columns are conditioned in three insulated chambers which can be heated to any desired temperature up to 400°. Controls for the flow of carrier gas are provided, and the progress of the conditioning is followed by thermistor detectors placed at the column exits.
W. T. CARTER

4058. **Effect of flow-rate and sample size on column efficiency in gas - liquid chromatography.** R. A. Bernhard (Dept. of Food Science and Technol., Univ. of California, Davis, U.S.A.). *Nature*, 1960, **185**, 311–312.—The efficiency of a column (10 ft. × 0·25 in. outside diameter) packed with 25% (w/w) of LAC-4-R777 (the succinate polyester of diethylene glycol) on firebrick at 100° is markedly dependent on the rate of flow of the carrier gas (helium), with an optimum value of 45 ml per min. with small samples. The optimum flow-rate increases and the efficiency decreases as the size of sample is increased.
A. R. ROGERS

4059. **Apparatus for the analysis of gaseous impurities in gases.** G. Seris, P. Vernotte, A.-M. Clave and P. Kohlmann (L'Air Liquide, Lab. Centr., Paris, France). *Chim. Anal.*, 1960, **42** (1), 28–32.—Small amounts of impurities in gases are concentrated to a level which enables them to be detected by a thermal-conductivity cell (described) for water, or an i.r. analyser for methane, or which enables them to be subjected to gas chromatography. Water is concentrated by passing the gas to be analysed at a known rate for 3 min. through a loop of polyethylene tubing immersed in liquid O, where the water condenses at the level of the liquid surface. When the loop is plunged into a water bath at 20°, the condensed water is released suddenly as a mist, which is carried without diffusion through the tube to the detector. The fact that the water is present as liquid droplets enhances the peak on the recorder and < 1 mg of water per cu. metre of gas can be detected. Methane is concentrated by absorbing the gas at −90° in a tube containing 170 mg of 5A

molecular sieve. To concentrate gases for chromatography, a mixture of 4A and 5A molecular sieves is used. The chromatographic apparatus is described and illustrated. E. J. H. BIRCH

4060. **Ionisation detector for gas chromatography.** S. Matoušek (Res. Inst. of Radiology, Prague). *Chem. Průmysl*, 1960, **10** (1), 16–21.—In the ionisation detector described, β-particles from ^{90}Sr are used as the source. The apparatus acts as an ionisation chamber with variable filling. The principal advantages of the instrument consist in its sensitivity and wide range of operating conditions. If quartz - Teflon is used for insulation, the detector can be used at temp. up to 250° to 300°. The quant. evaluation of the chromatograms can be carried out without previous calibration. It is suggested that by suitable modification the instrument could be used as a detector for integration registration, without the necessity for evaluating the chromatograms planimetrically. J. ŽÝKA

4061. **Automatic range changer for Beckman GC-2 gas chromatographs.** D. J. Darling, F. D. Miller, R. C. Bartsch and F. M. Trent (Res. Div., U.S. Industrial Chemicals Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 144.—The automatic range changer described continuously monitors the signal so that a max. on-scale peak height always occurs. With this device the unit is always run at max. sensitivity, the operator need not stand by to adjust the range, and no prior knowledge of the sensitivity requirements of any particular sample is necessary. Results indicate that peak-height measurements are not affected, although difficulty may be encountered in making area measurements. K. A. PROCTOR

4062. **Cathode-ray presentation of gas - liquid chromatograms.** R. P. W. Scott (Tech. Dept., Res. Sect., Benzole Producers Ltd., Watford, Herts., England). *Nature*, 1960, **185**, 312–313.—The micro argon detector of Lovelock is used in conjunction with an impedance converter of very low time-response, a normal television amplifier and power supply, and a 14-in. magnetically deflected cathode-ray tube coated with a phosphor of 200-sec. persistence. A mixture boiling over a range of $\simeq$ 100° can be quant. analysed in $\simeq$ 1 min. A. R. ROGERS

4063. **Simple apparatus for paper electrophoresis.** I. M. Raskin (Vitaminology Inst., Min. of Public Health, Moscow). *Lab. Delo*, 1960, **6** (1) 59–61.—In the apparatus described and illustrated, dry cells are used for the current supply and electrophoresis is carried out on a horizontal paper strip between two small baths containing the buffer soln. and electrodes. Results obtained in the determination of serum fractions compared favourably with those using conventional apparatus. A. BURWOOD-SMITH

4064. **Principles, development and application of two-dimensional electrophoresis.** H. Peeters and P. Vuylsteke. *Chem. Weekbl.*, 1959, **55** (49), 703.—The principles and the development of two-dimensional electrophoresis are discussed, and some applications of this technique are mentioned, *viz*, preparative electrophoresis of amino acids, polypeptides, proteins and other ions and the possibility of obtaining a rapid qualitative estimate of the electrophoretic and chromatographic properties of a mixture of ions. M. J. MAURICE

4065. **Synergic method of carrying out continuous electrochromatography.** S. R. Caplan (Nat. Chem. Lab., D.S.I.R., Teddington, Mddx., England). *Nature*, 1960, **185**, 378–379.—Ion-exchange membranes are used in place of paper to provide a stationary phase which is capable of highly selective sorption, within which particles would be immobilised with respect to eluent flow, but not with respect to current flow. The change from paper to membrane causes a change in the mobility ratios of solutes which differs from the change in retention volume ratios. In some systems, these changes are such as to give rise to synergy between electrophoresis and chromatography. A. R. ROGERS

4066. **Tri(hydroxymethyl)methylamine as an electrophoresis buffer.** R. D. Rapp and M. M. Memminger (The Reading Hosp., West Reading, Pa., U.S.A.). *Amer. J. Clin. Path.*, 1959, **31** (5), 400–403.—Tri(hydroxymethyl)methylamine buffer (**I**) improved the electrophoretic separation of serum proteins but the spots were not ideally shaped for planimetry; the use of a combination of **I** and barbitone buffer, of total ionic strength 0·07, gave a very satisfactory separation in one-half the time required with a standard barbitone buffer of ionic strength 0·1. P. NICHOLLS

4067. **Scanning of paper electropherograms after protein dyeing with bromocresol green.** A. Clark (Clin. Lab., West Wales Gen. Hosp., Carmarthen). *Nature*, 1960, **185**, 243.—The blue colour of protein that has been dyed with bromocresol green and developed by exposure to NH_3 vapour is not stable. A more stable colour is obtained when the dried dyed electropherograms are dipped in a soln. of diethylamine in diethyl ether (10%, v/v). G. P. COOK

4068. **Factors affecting albumin trailing during electrophoresis.** W. B. Yeoman (Frenchay Hosp., Bristol, England). *Clin. Chim. Acta*, 1960, **5** (1), 75–81.—Paper quality and thickness, applied voltage, and the no. of strips being run simultaneously are factors affecting albumin trailing. On Whatman No. 1 filter-paper at moderate voltage the trail represents between 9 and 14% of the total albumin. The method of correction previously applied (*Anal. Abstr.*, 1959, **6**, 4539) is confirmed. H. F. W. KIRKPATRICK

4069. **Electrophoretic apparatus with automatic registration of the extinction curve.** B. N. Zeliger (Leningrad Pediatric Inst.). *Lab. Delo*, 1960, **6** (1), 55–59.—An apparatus is described that combines a device for the paper electrophoresis of serum with a device for the automatic registration of the extinction curves of the separated fractions (a densitometer and automatic recorder). A. BURWOOD-SMITH

4070. **Starch electrophoresis. II. Starch column electrophoresis.** H. Bloemendal (Dept. of Biochem., A. van Leeuwenhoek-Huis, Netherlands Cancer Inst., Amsterdam). *J. Chromatography*, 1960, **3** (1), 1–10.—A review of apparatus, techniques and applications is presented with 26 references. It is stated that starch column electrophoresis is not so easily manipulated as block and gel methods, and offers no appreciable advantages. W. T. CARTER

4071. **Preliminary studies on quantitative zone electrophoresis in starch gel.** J. H. Pert, R. E. Engle, K. R. Woods and M. H. Sleisenger (New York

Hosp., Cornell Med. Center, N.Y., U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (4), 572–584.—A method for the standardisation of the buffer and soluble starch used in making the gel, a controlled procedure for staining, and the use of a reflectance densitometer for the determination of each separated protein fraction are described. Improved reproducibility and resolution are achieved. Results are compared with those obtained by boundary and other forms of electrophoresis and by ultracentrifugation, and the variation in patterns obtained with normal and pathological human sera is discussed.

W. H. C. SHAW

See also Abstracts—**3950**, Planimetric and densitometric measurements. **3976**, Thin-layer chromatography.

Optical

4072. **Design and performance of a rapid-scanning X-ray diffractometer.** A. Skertchly (Dept. of Textile Ind., Univ. of Leeds, England). *J. Sci. Instrum.*, 1960, **37** (1), 6–14.—The instrument described enables the equatorial diffraction intensity distribution from radially symmetrical specimens to be obtained over the Bragg angle range 0° to 20° in 20 sec. Sequential scans are performed at the rate of 2 per min., and the X-ray information is retained as pulses recorded on magnetic tape. The application to the analysis of phase transformations in high polymers of interest to the textile industry is described. G. SKIRROW

4073. **Use of Pyroceram crucible vials in ashing biological materials for spectrochemical analysis.** S. T. Bass and J. Connor (Dept. Agric. Chem., Michigan State Univ., East Lansing, U.S.A.). *Appl. Spectroscopy*, 1959, **13** (6), 158.—Pyroceram is a new glass material (Corning Glass Works) with a low thermal coeff. of expansion, high shock strength, good thermal conductivity, highly polished surface, ease of fabrication and resistance to corrosion by alkalis. Combined ashing and mixing vessels of this material are capable of withstanding an ashing temp. of 550° and the shock of a mechanical mixer. Advantages are the elimination of loss and possible contamination during transfer of ash from a crucible to a mixing container and saving in time.

P. T. BEALE

4074. **The sensitivity of spectrochemical analysis of solid samples and solutions.** E. Gegus (Res. Inst. for the Iron Industry, Budapest). *Magyar Kém. Foly.*, 1959, **65** (12), 469–471.—The sensitivity of spectrochemical methods is discussed. The use of solutions instead of solids can have many advantages and in suitable cases the sensitivity equals that of other methods. A. G. PETO

4075. **Advantages of a preliminary sintering of samples into buttons in the quantitative spectral analysis of crude samples.** T. M. Moroshkina and V. K. Prokof'ev. *Vestn. Leningr. Univ.*, 1959, No. 22, *Ser. Fiz. i Khim.*, (4), 132–135.—The value of the addition method in the determination of micro amounts of elements in crude samples is emphasised. This method requires that the element introduced shall be of the same chemical form as that in the sample. In the determination of Ti and Be, with additions of Ti and Be compounds different from those present in the sample, it is shown that sintering into a button in a reducing atmosphere in an electric furnace at 1200° to 1300° satisfactorily achieves this requirement. For Ti, the internal standard was Cr, and the line-pair (in A) Ti 4305·91 - Cr 4297·73 was used. For Be, the internal standards were Fe and Al, and the line-pairs used were Be 2348·61 - Al 2367·06, Be 3130·42 - Al 3082·16, Be 3131·07 - Al 3082·16, and Be 2348·61 - Fe 2343·49.

W. ROUBO

4076. **Precision of preformed versus laboratory-prepared graphite electrodes.** S. K. Brown (Aluminum Refining Co., Sheboygan Falls, Wis., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (6), 157.—Aluminium samples were sparked against factory-produced preformed graphite counter-electrodes and against electrodes shaped and re-shaped in the laboratory. The corresponding coeff. of variation indicate a marked superiority of the preformed electrodes (coeff. of variation $\simeq$ 0·5) against electrodes that had been shaped ($\simeq$ 0·8), then re-shaped after use ($\simeq$ 1·5) and re-shaped after being used again ($\simeq$ 3·0). It is suggested that possible causes are inconsistent dimensional tolerances, contamination and/or structural breakdown of the graphite after it has been sparked.

P. T. BEALE

4077. **Ignitor unit for d.c. arcs.** L. E. Owen (Goodyear Atomic Corp., Portsmouth, Ohio, U.S.A.). *Appl. Spectroscopy*, 1959, **13** (6), 158–159.—A simple circuit for d.c. arc ignition is given which does not require an r.f. transformer but which has the high-voltage (10 kV) secondary of the trigger transformer coupled in shunt with the arc gap. Component specifications are given.

P. T. BEALE

4078. **New electronic trigger unit for source units.** M. G. Seed. *Hilger J.*, 1960, **6** (1), 10–11.—A brief description is given of a trigger unit for capacitor discharges for spectrographic purposes in which the triggering action is controlled by a pulse delivered to the grid of a thyratron. Timing is sufficiently accurate to permit the study of time-resolved spectra. G. SKIRROW

4079. **Differential method of photometric analysis. I. Application to solutions containing one component.** S. D. Ross and D. W. Wilson (Sir John Cass Coll., London). *Analyst*, 1960, **85**, 51–54.—The differential spectrophotometric method of Reilley and Crawford (*Anal. Chem.*, 1955, **27**, 716) is adapted for use with the Unicam SP500 spectrophotometer. By this method an expansion of scale is obtained by means of a positive deviation from Beer's law. The method is applied to the analysis of one-component aq. soln. of the perchlorates of Ni^{2+}, Co^{2+}, Cu^{2+} and Cr^{3+}. The procedure for establishing the calibration graph is described. Results agree satisfactorily with those of gravimetric methods. A. O. JONES

4080. **Collaborative readings with the Cary-14 spectrophotometer.** J. M. Vandenbelt (Parke, Davis and Co., Detroit 32, Mich.). *J. Opt. Soc. Amer.*, 1960, **50** (1), 24–27.—Results of a collaborative study made with a group of nine Cary-14 spectrophotometers at various wavelengths in the ultra-violet (220 to 400 mμ) and in the near-infrared (0·75 to 2·6 μ) are given. U.v. data are also listed for a group of sixteen Cary-11 spectrophotometers. Acid $K_2Cr_2O_7$ standard soln. were used in the u.v. and Corning glass filters in the i.r. All sets of readings show significant amounts of variation. The standard deviations and coeff. of variation of

both types of instrument are similar, but smaller than those shown in earlier studies (*Anal. Abstr.*, 1956, **3**, 1567). The "14" is more consistent than the "11" at the ends of the wavelength range. The reproducibility of results using glass filters is substantially better than for soln. standards.

B. S. COOPER

4081. **A double-beam automatic prism - grating infra-red spectrophotometer.** L. W. Herscher (The Dow Chemical Co., Midland, Mich., U.S.A.). *Spectrochim. Acta*, 1959, (11), 901–908.—The apparatus described records infra-red spectra from 3800 cm^{-1} to 450 cm^{-1} with completely automatic programming of all the interchanges between the three gratings and the foreprism that form the optical system. The changeover points are controlled to avoid shifts in relative transmission, and no discontinuity is obvious. The scale is linear with wave number and is presented on a flat-bed roll-chart. The routine full run can be covered in 15 min. with automatic scanning speed suppression, and with $\simeq$ 1 cm^{-1} resolution. E. G. CUMMINS

4082. **Automatic slit drive for infra-red spectrometers.** D. F. Eggers, jun., and M. T. Emerson (Dept. of Chem., Univ. of Washington, Seattle, Wash.). *J. Opt. Soc. Amer.*, 1960, **50** (1), 11–13.—An automatic slit drive is described which gives constant spectrometer output over a wide range of frequencies. Values of the electrical circuit parameters are listed for application to the following prism materials—CaF_2, NaCl, KBr and CsBr.

B. S. COOPER

4083. **Infra-red micro-spectra of biochemical substances. I. Modification of Perkin - Elmer 12-C spectrometer with microscope for linear wavelength recording at level energy input.** H. L. Dinsmore (Bethel Coll., St. Paul, Minn., U.S.A.). *Spectrochim. Acta*, 1959, **15** (12), 1025–1031.—Design data are given and modifications are described for the conversion of the Perkin - Elmer 12-C Spectrometer into an instrument having a linear wavelength scale and a nearly level input energy throughout the NaCl prism region. Examples of i.r. spectra of micro samples (<20 μg) using a reflecting microscope and the modified instrument indicate a significant improvement in the presentation of the spectra.

II. Pressed KBr micro-pellets for use with reflecting microscope. H. L. Dinsmore and P. R. Edmondson. *Ibid.*, 1959, **15** (12), 1032–1035.—For the preparation of transparent pressed KBr pellets containing biochemical substances, using as little as 0·1 to 0·4 mg of KBr and a few μg of the biochemical material, a special press is described. This consists of a steel ball fitting into a depression in a Lucite die. The procedure is described. Examples of recorded i.r. spectra, obtained with these transparent pellets in conjunction with a Perkin - Elmer reflecting microscope (model 85) and a modified 12-C spectrometer, are given.

G. P. MITCHELL

4084. **Spectra - structure correlations for the near-infra-red region.** R. F. Goddu and D. A. Delker (Hercules Powder Co., Res. Center, Wilmington, Del., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 140–141.—Spectra - structure correlations, average molar absorbance data and spectral data on useful solvents for the near-infra-red region are tabulated.

K. A. PROCTOR

4085. **Laue spectrometer for multi-channel X-ray spectrochemical analysis.** J. Ladell and N. Spielberg (Philips Lab., Irvington-on-Hudson, New York, U.S.A.). *Rev. Sci. Instrum.*, 1960, **31** (1), 23–29.—A method is described for using the Laue diffraction technique in multi-channel X-ray spectrochemical analysis. A compact instrument with no moving parts is constructed by using a single analysing crystal with individual detectors for simultaneous registration of the relative amounts of the elements in the sample to be analysed. G. SKIRROW

4086. **Glass colour standards and a uniform chromaticity scale for sugar products.** B. A. Brice (Eastern Regional Res. Lab., U.S. Dept. of Agric., Philadelphia, U.S.A.). *J. Opt. Soc. Amer.*, 1960, **50** (1), 49–56.—Colour specifications are given for the official glass colour standards, used for the rapid classification of samples according to chromaticity, for extracted honey, maple syrup (*cf. Anal. Abstr.*, 1956, **3**, 3190), sugar-cane syrup and sugar-cane molasses. These standards are used for classifying samples into broad groups and do not provide a method of determining colour. A proposal is made for establishing forty-five glass colour standards lying uniformly along a single-number chromaticity scale as a reference scale for sugar products. B. S. COOPER

4087. **New reflectometer and its use for whiteness measurement.** R. S. Hunter (Hunter Associates Lab., McLean, Virginia, U.S.A.). *J. Opt. Soc. Amer.*, 1960, **50** (1), 44–48.—With the instrument described, readings taken with green and with blue tristimulus filters enable an assessment to be made of the whiteness of white and near-white paints, papers, textiles, plastics and porcelain enamels. An ultra-violet-absorbing filter in the instrument may be placed in either the sample-viewing or incident-light beams to include or exclude the near-ultra-violet radiation which excites fluorescence. This leads to a measure of the contribution of fluorescent brightening agents to blue reflectance, and hence to whiteness, of the sample.

B. S. COOPER

4088. **Multi-function automatic recording photometric titrator.** P. W. Mullen and A. Anton (Textile Fibers Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 103–106.—The instrument described is suitable for colorimetric, nephelometric, and chemiluminescent indicator titrimetry. It is assembled from a Precision-Dow recording potentiometric titrator, a modified Beckman Model B spectrophotometer, and necessary intermediate electronic components. The extinction of the soln. is plotted directly against vol. of titrant added and the accuracy and precision compare with those obtained by manual titration. K. A. PROCTOR

See also Abstract—**3636**, Micro-coulometer.

Thermal

4089. **Burner for combustion of large solid samples.** L. L. Farley, F. L. Detert, S. W. Nicksic and W. P. Webb (California Res. Corp., Richmond, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 142–143.—A burner is described which will burn 20 to 50-g samples of fusible solids in $<$ 30 min.; it has been applied to the determination of S, Cl, Br and F. Materials that leave non-volatile residues containing the desired element cannot be used with this burner. K. A. PROCTOR

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{2+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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